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MANUFACTURING TECHNOLOGY (MATES) II

Task Order 0006: Air Force Technology and Industrial Base Research

Sub-Task 07: Future Advances in Electronic Materials and Processes - Flexible Hybrid Electronics

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14. ABSTRACT
This report documents the findings of a study of the U.S. electronics manufacturing industry, including an integrated assessment focused on projected advances in electronics materials and processes and their implications for military aerospace applications. A major goal of the study was to understand trends, manufacturing issues/barriers, enabling technologies, and investment opportunities with significant potential for payoff in the context of future electronics product capabilities, especially for military aerospace applications. While the work covered the U.S. electronics industry in general, it placed special emphasis on flexible hybrid electronics (FHE) as an emerging and promising industry. The analysis addressed latest developments in inorganic and organic materials for specialty applications, including recent developments in 2D materials such as graphene for electronics applications. For both conventional electronics and FHE, the study included a review of materials, manufacturing processes, packaging technologies, design tools, and current and proposed applications, and identification of technology gaps and opportunities for investment. For conventional electronics, it also addressed computational tools for design of resilient electronics for severe environments. For the emerging field of FHE, the report includes estimates of future trends in applications and the technologies that are expected to enable them.

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1.0 EXECUTIVE SUMMARY

This report documents the findings of a study of the U.S. electronics manufacturing industry, with a particular emphasis on flexible hybrid electronics (FHE). The project aimed to perform an integrated assessment focused on projected advances in electronics materials and processes over the next 25 years and their implications for military aerospace applications. The study was conducted by a Universal Technology Corporation (UTC) team, as part of the Manufacturing Technology Support (MATES) II Program, Task Order 0006, entitled "Air Force Technology and Industrial Base Research and Analysis," under the sponsorship of the Air Force Research Laboratory, Manufacturing and Industrial Technologies Division, Electronics and Sensors Branch (AFRL/RXME). The study team comprised researchers from UTC, the Georgia Institute of Technology Research Institute (GTRI), and Ohio University, and also included Mr. Arthur Temmesfeld, who acted as an independent consultant to provide industrial base analysis support.

A major goal of the study was to understand trends, manufacturing issues/barriers, and enabling technologies in the context of future electronics product capabilities, especially for military aerospace applications. While the study and its final report addressed the U.S. electronics industry in general, this supplemental report only contains the sections of the final report pertaining to FHE.

In essence, FHE is a combination of conventional inorganic semiconductor circuits and microelectronics fabrication processes and packaging with rigid or flexible, organic or inorganic electronic components and techniques for digital functional printing on rigid or flexible substrates. A more thorough discussion of various definitions for FHE and related technologies is included in this report.

One key concern for the U.S. electronics industry, and for defense electronics in particular, is that while significant research and development in electronics occurs domestically, much of the manufacturing strength for electronics products resides overseas. The emerging FHE field is not currently the exception. [1] This tendency for stronger foreign manufacturing of electronics implies that U.S. defense organizations must actively work to ensure the availability of domestic suppliers and improve their capability to meet the demand for increasingly sophisticated defense electronics. This report addresses state-of-the art and emerging electronic materials and processing technology from the point of view of the U.S. industrial base with special emphasis on FHE.

The performance of electronic systems, both military and civilian, has indisputably grown at an impressive rate since the birth of the electronics field. This is due in great part to continued improvements in miniaturization of electronic components and systems, and the resulting reduction in the size, weight, and power (SWaP) required to implement functions of increasing complexity, in addition to progress in inorganic semiconductor materials that can outperform silicon in speed and power. However, miniaturization and advances in inorganic materials are not expected, at least not by themselves, to enable the next revolution in electronic systems and applications. The next wave of revolutionary progress in electronics will greatly rely on easily customizable electronic devices and systems that can be quickly and affordably (that is, flexibly) manufactured and integrated, possibly conformably, using a variety of deposited materials on a variety of multifunctional substrates. Mechanical flexibility will be a desired characteristic for many applications, but flexibility in manufacturing is vital for this new wave of electronics.

Around the world, industry and academia, often with government support, have continuously made progress for decades in materials and processing technologies for electronics. Recent progress seems to indicate that the desired flexibility in manufacturing of electronics systems is indeed attainable. For example, the development of inks, printing processes, and roll-to-roll capabilities for manufacturing of electronics is a current reality. [2] Also, a variety of electronic packaging designs have been researched and developed that combine high performance rigid and/or flexible inorganic electronics devices with organic materials on flexible substrates.

However, significant development is still necessary before the performance and reliability of FHE products can approach those of systems produced using conventional electronics manufacturing. For instance, in spite of significant progress in materials and processes, organic semiconductors are not yet capable of the high charge carrier mobility and high power capacity required for uses beyond the pervasively proposed but not yet widely successful conformal, printed large-area display, photovoltaic, and sensors applications. [2]

Even after achieving the performance and reliability characteristics demanded by initial applications, FHE systems for military use will have to satisfy more stringent requirements than those expected for consumer applications. [3] For example, appropriately designed and applied coatings can help protect the integrity of FHE systems in severe environmental conditions of temperature and humidity. Military applications also make it necessary to account for vibration, shock, and similar environmental challenges. [4] In addition, common flexible substrate materials are not compatible with fabrication processes that require elevated temperatures, and therefore development of more resilient substrate materials is required.

In spite of current shortcomings, FHE as an emerging industry has grown steadily in the last few years, and its application domains are expanding. Forecasts for the growth of the flexible (printed and hybrid) electronics market are abundant and vary widely, and each of them focuses on particular needs, technologies, and agendas. Regardless of the differences in these predictions, it is clear that printed electronics, flexible electronics, and their combinations are expected to expand rapidly. Moreover, the adaptation of conventional (e.g., CMOS) electronic technologies to flexible substrates and packaging will enable FHE use in applications beyond those possible with conventional electronics. That is expected to create significant market demand for FHE technologies and therefore increase market growth predictions for flexible and printed

electronics as partial enablers of FHE. Nevertheless, there are challenges and opportunities that the FHE industry must overcome and seize in regards to heat dissipation; resilient, flexible substrates; limited power supply and physical space; 3D integration; photonics integration; and flexible packaging; among others, before FHE can become a ubiquitous technology.

While this study was underway, the U.S. Federal Government competed and awarded a contract for the creation of an FHE institute to be part of the National Network for Manufacturing Innovation. The FlexTech Alliance, a consortium of a large number of domestic industrial and academic organizations, was the recipient of the contract award for the Flexible Hybrid Electronics Manufacturing Innovation Institute (FHE MII). NextFlex, as the institute has been named, has started to structure and perform work toward achieving U.S. excellence in FHE. [5] From the Government side, the institute is managed by the U.S. Army with participation from other services, in particular the U.S. Air Force. This report is expected to help inform government, academia, and industry personnel on the current areas of investments and developments for electronics and FHE, and on promising areas for near term investment. Given that goal, the report may also help inform the initial stages of development for the FHE MII.

2.0 INTRODUCTION

The electronics industry has made dramatic progress since the discovery of radio waves and the invention of the telephone in the late 1800s. The invention of the vacuum tube around 1907, the transistor near 1925, and the integrated circuit (IC) circa 1950 propelled revolutionary developments that have resulted in a pervasive use of affordable electronic systems, many of them as commodities, for a variety of applications including communications, computing, information technology, transportation, science, health, and defense. Ever improving miniaturization of electronic devices has also resulted in reductions in cost and SWaP requirements, which have enabled previously unimaginable system performance for both military and non-military applications.

The purpose of this study is to develop an integrated assessment of the U.S. domestic electronics industry, with a particular emphasis on flexible hybrid electronics (FHE), focused on projected advances in materials and processes in the near future and their implications for military aerospace applications. This is being accomplished through analysis of a representative subset of the electronics industry to understand trends, manufacturing issues/barriers, and enabling technologies that will increase future product capabilities, especially for military aerospace use.

Flexible hybrid electronics (FHE) is currently considered a field with great potential for worldwide growth in both technology development and applications. To a large extent, FHE manufacturing utilizes existing printing methods with appropriate ink formulations. In the case of large area printing of electronic devices, FHE also benefits from roll-to-roll (web-based) production methods and equipment.

This introduction describes the methods, assumptions, and procedures followed throughout the study, and then presents a few necessary definitions for FHE technologies. The body of the report provides a practical description of this promising emergent industry and of how it uses conventional technology and new developments. It covers materials, processes, packaging, design, applications, and markets for FHE. For each of these aspects, the report attempts to describe the state of the technology and the business implications, including financial risk. It also provides estimates of future directions.

2.1 Methods, Assumptions, and Procedures

To facilitate the research effort and the presentation of findings, the study team divided the electronics industry into two main categories: conventional electronics and FHE. This supplemental report documents results related to FHE technologies. Even though the processes used in FHE are currently somewhat different from and more diverse than those used in conventional electronics, the boundaries between the two electronics technology areas will likely be less defined in the future, for several reasons that include : (1) the vast knowledge and continued development in electronics materials and manufacturing processes, (2) the commonality of application areas and users, (3) the fact that many companies are expected to develop and market products in both conventional electronics and FHE, and (4) the fact that FHE technologies may substitute some of their conventional equivalents because of cost benefits.

Examples of FHE substituting conventional electronics may include: (1) production of flexible printed circuit boards, and (2) packaging of small form factor electronics by adapting CMOS

technologies into flexible devices. Electronics as a whole has and will continue to enable many technological developments, independently of how electronic systems are designed and built.

Due to the large number of companies involved in the electronics industry and the fact that FHE is still unstable as an industry, the study focused on a representative set of companies instead of attempting to cover all industry participants.

Several methods were employed in this study for gathering technology and market data:

1. <u>Open literature search</u>. This consisted mostly of research of company and defense organizations' websites to identify current status and plans for requirements and development, but also included a review of academic-type publications when the level of detail necessitated it. Key goals of this literature search were to
   a. Identify key participants in today's electronics industry
   b. Identify companies/facilities/processes that are of interest to defense applications
   c. Describe university/corporate/government (e.g., DOE or NSF) sponsored research that represents future trends
2. <u>Conferences / interviews</u>. To help gather relevant current information, team members attended several conferences: (1) 2014 Defense Manufacturing Conference; (2) 2015 Flexible and Printed Electronics Conference; (3) 2015 Government Microcircuit Applications and Critical Technology Conference; (4) 2015 Military Communications Conference; and (5) 2015 Printed Electronics Conference. Technical sessions, and discussions with representatives from many organizations, allowed the team to gather relevant information regarding current and future developments in electronics.
3. <u>Analyses by the Industrial Base Information Center (IBIC)</u>. IBIC is a contractor-operated center supported and managed by the Manufacturing & Industrial Technologies Division at the AFRL Materials and Manufacturing Directorate. Its objective is to provide assessment of the financial, market, and technology status of various companies in various segments of the domestic manufacturing industrial base. This study utilized business-type assessments from IBIC to complement findings on new and upcoming electronics science and technology developments. The combination of in-depth business and technology findings provided a more clear understanding of the industrial base than what was achievable by only studying one or the other.

This research effort benefited from the existence of domestic and international organizations with focused efforts on promoting technology and business progress in the electronics industry. Table 1 lists some of these organizations and describes their charters.

Table 1. Domestic and International Organizations for Electronics

Organizations that Promote Progress in Electronics Technology and Applications	
Organization / Website	**Characteristics**
InterNational Electronics Manufacturing Initiative (iNEMI), www.inemi.org, Herndon, Virginia, USA, Asia (Shanghai and Tokyo) and Europe (Limerick, Ireland)	• not-for-profit R&D consortium of approximately 100 leading electronics manufacturers, suppliers, associations, government agencies, and universities • roadmaps the future technology requirements of the global electronics industry • helps eliminate technology and infrastructure gaps through timely, high-impact deployment projects
Organic and Printed Electronics Association (oe-a), www.oe-a.org	• leading international industry association for organic electronics and printed electronics • represents the entire value chain of this emerging industry • promotes the establishment of a competitive production infrastructure for organic electronics and printed electronics
FlexTech Alliance, www.flextech.org, San Jose, California, USA	• fosters the growth, profitability, and success of the flexible and printed electronics supply chain, and its application areas • offers expanded collaboration between and among industry, academia, and research organizations for advancing flexible, printed electronics from R&D to commercialization.

Of these organizations, the iNEMI was of particular importance. The iNEMI was created in 1995 as a North-American industry initiative with participation from government and academia. Its immediate roots were two other efforts that had as their underlying objective “to recapture American leadership in electronics manufacturing.” [6] In 2003, iNEMI’s scope was expanded to the global electronics supply chain. Today’s iNEMI is a global “industry-led consortium that is advancing electronics manufacturing technology.” [7]

Roadmaps for semiconductors have been developed since as early as the late 1970s or early 1980s. [8] Since its inception, iNEMI has been regularly developing technology roadmaps for semiconductors. At least since 1999, iNEMI has been publishing a new edition of its roadmap on odd numbered years and an update on even numbered years. The 2015 iNEMI Roadmap edition divided the electronics industry into the product groups described in Table 2. The focus of the present study is on products for aerospace / defense applications, which naturally include networking and communications systems. Analysis and forecasting of the defense electronics portion of the industry requires some understanding of the forces driving the electronics industry as a whole, particularly in regards to development of new materials and processes.

Table 2. Product Groups from the 2015 iNEMI Roadmap [9, p.9]

Electronics Product Sectors Identified by iNEMI in the 2015 Roadmap	
Industry Sector	**Product Characteristics**
Aerospace / Defense	Products that must operate reliably in extreme environments.
Automotive	Products that must operate in an automotive environment.
Consumer Stationary/ Office Systems	Driven by the need for maximum performance over a wide range of cost targets.
High End Systems	Products that serve in high-performance computing, server, data storage, networking, data communications, and telecommunications markets.
Medical	Products that must be highly reliable and, in some cases, support life-critical applications.
Portable / Wireless	Produced in high volumes, and cost is the primary driver. Hand-held, battery powered products are also driven by size and weight reduction.

iNEMI has been devoting an entire chapter of its roadmap to Large Area Flexible Electronics since 2011. For 2013, that chapter covered the technologies that are critically necessary for commercial launch and market diffusion, presents a snapshot of the current industry, and describes recent innovations and trends. [10] In its introduction, the large area flexible electronics (LAFE) chapter lists a number of important business issues, starting with market driven realignment of various companies and the FHE products that they offer or plan to offer. Their description of the current business situation implicitly indicates that companies and consortia with government support in Europe and Asia seem to be leading the LAFE technology area, while governmental organizations (NIST and DARPA) and non-profits (e.g., FlexTech Alliance) push development in the U.S. The most recent iNEMI Roadmap, published in January 2015, reviews the most critical technology developments required for commercial success of LAFE. Since FHE shares many of the technologies required for LAFE, the considerations and conclusions presented in the iNEMI Roadmap are broadly applicable to FHE.

This report is divided into 9 main sections. The Executive Summary and this Introduction are sections 1 and 2, respectively. Sections 3 and 4 address FHE materials and manufacturing technology developments, respectively, that will be critical for the satisfaction of existing and new application requirements. Sections 5 and 6, respectively, describe innovations in packaging and design tools for FHE technology. A discussion of capabilities, devices, and applications enabled by FHE is presented in section 7, followed by an analysis of the FHE industry in section 8. Section 9 describes Conclusions and Recommendations. While not included in this supplemental FHE report, the final report for the entire study also contains sections that present conventional electronics technologies from a point of view similar to that used for FHE, with the purpose of describing the evolution of conventional electronics, and introducing the state of the art in the conventional electronics industry.

In most cases, this report clearly identifies technology gaps and development opportunities by presenting them within boxes between paragraphs. The reader is advised to also look for other technology gaps and opportunities identified by headings and lists throughout the report.

2.2 Definitions

"*Flexible electronics* refers to technologies that enable flexibility in the manufacturing process as well as flexibility as a characteristic of the final product". [3] Flexibility in the manufacturing process is achieved, for example, from the fact that technology for printing electronics is capable of providing on-the-fly customization of products. That is the case with radio frequency identification (RFID) devices, contactless smart cards, and smart labels that are produced using roll-to-roll printing processes. The computer-controlled printing process gives each printed device its unique identifying characteristic or code. [11] Manufacturing flexibility can also stem from the ability to combine traditional semiconductor manufacturing methods with printed electronics to produce a given device or system.

In the world of electronics, the term *hybrid* has been used for conveying a number of different meanings. The following list captures the connotations of the word hybrid that are relevant to this report.

1. *Hybrid [electronic] circuits* are circuits in which [active] chip devices such as "transistors, diodes, integrated circuits, chip resistors, and capacitors" are "electrically interconnected on an insulating substrate on which" "conductors or combinations of batch fabricated components such as conductors, resistors, and sometimes capacitors and inductors have previously been deposited". [12]
2. *Hybrid electronics* can refer to a few different concepts:
    a. A combination of through-hole and surface-mount technology in the same printed circuit board (PCB)
    b. An assembly that "looks like a printed circuit board, but contains some components that are electrochemically grown onto the surface of the substrate rather than being placed on the surface and soldered" [13]
    c. A combination of traditional semiconductor wafer-based microelectronics fabrication methods and printed electronics methods
    d. A combination of inorganic and organic materials to fabricate an electronic device
    e. A combination of traditional semiconductor wafer-based microelectronics technology with nanomaterials to fabricate an electronic device; an example is the use of CMOS technology and carbon nanotubes (CNTs) to fabricate fast, non- volatile random access memory (RAM) [14]
    f. A combination of electronic and photonic devices in a single, integrated package
    g. A flexible substrate with mounted rigid and flexible electronic devices. The literature offers several definitions for FHE:

1. Systems with "organic/polymeric and inorganic flexible devices integrated to intrinsic and hybridized systems" [1]
2. Systems "combining printed and flexible electronics with classical silicon components which enables a bigger range of new applications" [15]

3. "Combinations of processing including large-area photolithography, screen printing or printed circuit board (PCB) technologies that make use of flexible substrates (e.g., polymer films on paper)" [2]
4. A "combination of conventional silicon circuits with organic electronic components and digital functional printing techniques" [2]

The term *functional printing* is used here to mean "the deposition of a printable substance that engenders an active or passive functionality beyond traditional graphical media. The resultant product will have unique form and function to sense or control conductivity, resistivity, thermo-chromic reactions, fluid dynamics, or chemical processes". [16] *Digital printing* refers to methods that print directly from a [digital] computer file as in inkjet or laser printing. Therefore *digital functional printing* refers to methods for printing functionality beyond graphics directly from a computer file.

2.2.1. FHE Definition by Aggregation

None of the available definitions for FHE sufficiently and comprehensively describes this technology and industry. However, by appropriately combining these definitions it is possible to arrive at the following, more general definition used for the remainder of this report:

Flexible Hybrid Electronics (definition by aggregation): Refers to devices, systems, and processes that combine conventional rigid inorganic semiconductor materials, circuits, fabrication, and packaging processes with innovative features such as organic materials, mechanically flexible devices and substrates, and/or digital functional printing techniques.

In essence, this definition refers to materials (organic versus inorganic, flexible versus rigid) and processes (conventional, such as photolithography, or innovative, such as large area digital printing). Conventional electronics consists of inorganic materials, rigid devices, and traditional processes. Non-conventional electronics can use organic materials; flexible components, substrates, or devices; digital functional printing; and other innovations. An FHE system or process combines at least one attribute from conventional electronics with at least one attribute from non-conventional electronics. In addition to suggesting possible mechanical flexibility (compliance) of electronic devices or assemblies, the word flexible in FHE denotes adaptability of the manufacturing process to enable, for example, large area printing, customization, reduced costs, and/or reduced environmental impact.

2.2.2. FHE Definition for FHE Manufacturing Innovation Institute

In August 2015, the U.S. Secretary of Defense announced the award of a contract for the creation of the Flexible Hybrid Electronics Manufacturing Innovation Institute to a consortium of 162 companies, universities, and non-profit organizations led by the FlexTech Alliance. [17] This institute, which is part of the National Network for Manufacturing Innovation, is managed by the Department of Defense (in particular the US Army with support for other services including the US Air Force). The DoD notice of intent to launch the competition for the institute stated that "FHE are enabled through innovative manufacturing processes and fabrication that preserve the full operation of traditional electronic devices on flexible, stretchable and conformal circuit

boards that can be attached to curved, irregular and often stretched objects". [18] The slides from the Proposer's Day Meeting in February 2015 provide the following definition. [19]

<u>Flexible Hybrid Electronics</u> (FHE MII Definition): Highly tailorable devices on flexible, stretchable substrates that combine thinned CMOS components with components that are added via "printing" processes. This technology is identified as flexible-hybrid due to integration of flexible components such as circuits, communications, sensors, and power with more sophisticated silicon-based processors.

This definition represents a subset of the general definition provided in Section 2.2.1; there is no conflict between the two definitions. While the remainder of this report covers FHE technology that satisfies the general definition of Section 2.2.1, much of the technology covered actually falls under the definition provided for the institute. It is clear from the context when the technology being described goes beyond the institute definition. That is the case, for example, with rigid ICs mounted on flexible substrates.

As part of the 2016 FLEX Conference, the FlexTech Alliance is hosting short courses on various topics, one of which is Flexible Hybrid Electronics. That course is expected to describe three approaches to FHE manufacturing: (1) chip-on-flex; (2) micron scale thin-film devices on flex; and (3) sub-micron scale self-assembled/imprinted device based coatings on flex. The chip-on-flex approach, which consists of the adaptation of CMOS ICs on flexible substrates, is covered in Section 7.3.4 of this report. The other two approaches are not based on adaptation of existing conventional electronics, but on advances in printed electronics. Micron-scale thin-film devices on flexible substrates involves generally "larger" (in the sense of microelectronics) printed electronic elements such as passive R, L, and C components and antennas, which may not need high resolution printing capabilities. These devices can improve performance mainly by reductions in size and weight and elimination of rigid packaging. Micron-scale devices are discussed throughout this report. Sub-micron scale self-assembled/imprinted device based coatings on flexible substrates consist of more elaborate devices with nano-coatings that, for example, can improve sensor or solar cell responses. They may also involve assembly techniques that demand more advanced printing capabilities. Most of the technologies that implement this third approach are in the R&D stage and are expected to impact FHE in the long term. These future advances are also discussed throughout this report.

3.0 ADVANCES IN FHE MATERIAL TECHNOLOGIES

In principle, all materials that have been traditionally used for conventional electronics are also available for use in flexible hybrid electronics (FHE) devices, systems, and processes. In actuality, some materials are easier to process and/or result in better properties than others. One of the main debates regarding materials for FHE applications is the use of traditional inorganic materials or innovative organic materials. Advantages and disadvantages of both are described throughout this section. Section 3.1 provides a brief sample of the different ways that inorganic materials can be used for FHE technologies. For example, Section 3.1.1 gives an introduction to the various research avenues that exist for making traditional inorganic silicon semiconductor technology mechanically flexible; more detailed information on how these processes are carried out can be found in Section 4.2. Section 3.2 provides an introduction to the various organic materials that are now being considered for electronics applications, with particular emphasis on carbon-based technologies, since a considerable amount of research is being conducted involving these technologies. Additionally, within both organic and inorganic materials, nanomaterials have emerged as a leading research area for FHE. Specific information regarding nanomaterial technologies, including inorganic nanoparticles (Section 3.1.2), graphene (Section 3.2.2), and carbon nanotubes (CNTs) (Section 3.2.3), among others, is dispersed throughout Section 3.0.

Sections 3.1 and 3.2 are intended to provide a brief introduction to the various material systems that are being considered for FHE; additional detailed descriptions of all of the technologies mentioned in Sections 3.1 and 3.2 can be found throughout Section 3.0.

FHE commonly manifests itself in the form of an organic or inorganic material being coated, deposited, or printed onto a flexible substrate. While traditional deposition methods typical of conventional electronics manufacturing can also be used for FHE (as will be seen in 4.1.2.2), printing and coating technologies are becoming more popular because their low-temperature characteristics make them more compatible with flexible substrates of interest. Therefore, because printing/coating techniques are gaining steam in the industry, the materials applied to substrates to create FHE are often in the form of inks, where the functional electronic material (conductor, semiconductor, dielectric, etc.) is mixed with solvents and other components to create a printable/coatable composition. Consequently, a large portion of Section 3.0, specifically Section 3.3, is dedicated to FHE ink technologies. Some of the inorganic and organic materials briefly introduced in Section 3.1 and Section 3.2 will also be addressed in portions of Section 3.3, as these materials can be used to create functional ink formulations. As mentioned, FHE often involves a functional material being deposited onto a substrate material. These substrates can have forms that range from rigid to flexible, and are made from a variety of materials, depending on the intended application. Therefore, a detailed discussion of the various types of substrates used for FHE, which include ceramic, paper, plastic, and glass, among others, and the advantages and disadvantages of each, will be addressed in Section 3.4.

3.1 Inorganic Semiconductors/Materials for Printed Electronics

A large amount of speculation exists regarding whether organic materials will replace inorganic materials in the future of electronics. [20] While organic materials seem to be gaining speed and are continually researched by universities and corporations around the world, there are still several areas where they fall short of inorganics. First of all, inorganic materials comprise the current technology. Therefore, there are countless manufacturing facilities in place that function

today producing electronics based on inorganic technology. Needing to create new manufacturing facilities in order to produce organic electronics would be a significant expense and time commitment, and this disadvantage could outweigh all of the advantages of organic materials. Organic materials would gain popularity if the existing manufacturing facilities only have to be slightly modified to have the capability to produce organic electronics. Section 3.1 will summarize ways that traditional inorganic materials are being used for innovative flexible electronics, including wafer thinning and exfoliation processes (Section 3.1.1) and functional inorganic nanoparticle ink formulations (Section 3.1.2).

3.1.1 Flexible Devices from Traditional Semiconductor Processes

Organic materials are also up against the latest innovations in conventional electronics. Research and development (R&D) efforts on fabrication of flexible semiconductor devices from inorganic (mostly silicon) materials and conventional semiconductor manufacturing processes are also underway. Researchers from Lehigh University in Bethlehem, PA, published a paper that discussed the electrical consequences of mechanically straining a polycrystalline silicon thin film transistor (TFT) by bending the material from -1.2% to 1.1%. [21] In this study, the flexible silicon TFT was fabricated by temporarily attaching the polymer foil substrate to a rigid substrate, such as silicon wafer or glass. Then, conventional manufacturing steps were carried out, including deposition and etching, to create the TFT. After fabrication, the polymer foil was detached from the rigid substrate to create a flexible silicon TFT. As part of their study, the researchers discovered that the electron mobility of the material increased under tensile forces and decreased under compressive strain. The hole mobility of the material demonstrated the exact opposite trend. Additionally, in both the n-type and p-type polycrystalline silicon TFTs, the off current decreased under tensile forces while it increased under compressive strain.

Overall, the study at Lehigh University demonstrated that while the change in device characteristics caused by mechanical strain should be taken into account when designing a flexible electronics device and that much further research needs to be performed to understand the exact mechanisms that are occurring, all of the TFTs tested during the experiment remained functional over the entire range of the applied strain and no obvious physical damage was observed. American Semiconductor, a company located in Boise, ID, is the leader in flexible integrated circuit (IC) and flexible silicon technology.

In 2011 at the Flexible Electronics & Displays Conference, American Semiconductor presented the industry's first demonstration of a wafer scale process for high performance, flexible, single crystalline complementary metal-oxide semiconductor (CMOS) circuits. [22] Their technology, called FleX™ Silicon-on-Polymer, is a process that creates high performance, single crystalline CMOS circuits with multi-layer metal interconnect on a flexible substrate. This post-fabrication process can be applied to silicon-on-insulator (SOI) processes from any foundry to create flexible silicon wafers with thicknesses less than 2000 angstroms on top of a polymer substrate.

American Semiconductor is an award-winning company and is recognized as the industry pioneer for flexible ICs. Their technology is unmatched and provides significant value in the FHE world today as it takes advantage of conventional, high-performance single-crystalline CMOS instead of nanoparticle inks or lower-performing organic materials. Some researchers are taking these alternative fabrication approaches a step further by creating flexible silicon materials

and devices without the need for a polymeric supporting substrate. [23] Some of these processes include grinding the wafer down to remove 99 percent of the silicon or exfoliating off the very top layers of the wafer, both of which enable conventional silicon wafers to become mechanically flexible simply by removing a majority of the supporting wafer.

More information on techniques used to make traditional silicon electronics more flexible, including grinding, exfoliating, and American Semiconductor's FleX™ process, can be found in Section 3.3. The various FHE applications that utilize these flexible conventional silicon technologies are described in Section 7.0.

3.1.2 Inorganic Nanoparticle Materials

In addition to making traditional inorganic silicon-based electronics mechanically flexible through various processing techniques, inorganic nanoparticle inks can be applied to a variety of substrates in order to create flexible inorganic electronics. [24] For example, metal nanoparticles, such as silver nanoparticles, are often used to formulate conductive inks for printed electronics applications. Countless companies exist that have commercialized this type of technology, which is discussed further in Section 3.3.3. Inorganic semiconductor nanoparticle inks exist as well, but they are not as well established in the market compared to conductive metal nanoparticle inks. [25] One of the first companies to create this technology is NanoGram Corporation, who, in 2009, fabricated the first TFT produced with inorganic semiconducting ink that contained crystalline silicon nanoparticles. Other companies, such as Nanograde, produce various kinds of semiconducting nanoparticles that can be incorporated into ink formulations. [26] More detail regarding this technology can be found in Section 3.3.7.

Similarly, dielectric nanoparticles, such as silicon dioxide nanoparticles, can be used to create dielectric ink formulations (see Section 3.3.6). Inorganic nanoparticles and ink technology offers significant benefits compared to traditional photolithography methods used to create conventional inorganic electronics and to organic materials used for FHE. [24] First, inorganic nanoparticle inks enable printed electronics, which are cheaper, faster, and more environmentally friendly compared to conventional electronics manufacturing methods. Inorganic nanoparticle inks can also be printed on a wide variety of unconventional substrates, allowing for the creation of mechanically flexible electronics. Second, inorganic nanoparticle inks enable higher performing flexible electronics because inorganic materials have innately better electrical properties compared to organic materials, which are discussed below. However, inorganic nanoparticles have disadvantages as well. [24] When dispersed in a solvent to create an ink, inorganic nanoparticles have a tendency to aggregate and form clumps, which then clogs printing and/or coating equipment. Additives can be used to prevent or minimize aggregation, but unfortunately the additives also decrease electrical performance. Additionally, many inorganic nanoparticle formulations, especially conductive metal nanoparticle inks, need to undergo post-treatment processes. Many times these processes require high temperatures, which negatively affect ideal substrates for flexible electronics, such as paper and plastic. Detailed descriptions of the various types of inorganic nanoparticle inks for flexible electronics applications can be found throughout Section 3.3.

3.2 Organic Semiconductors/Materials for Printed Electronics

Despite the existing manufacturing facilities designed for inorganic materials and the current innovations in conventional electronics, organic materials and electronics will find their place. [20] Organic and polymer electronics will not replace the current technology in high-performance applications due to their lower intrinsic electrical capabilities, but they can pursue applications where their qualities give them an upper hand compared to current technologies. For example, polymers have advantages in the areas of processability and flexibility that are unmatched by inorganic materials. Organic materials are easily coated, even to large-area surfaces. Therefore, they are ideal for high-volume production of commodity and/or large-area products. Currently, a large amount of research is being invested in the use of organic electronics for lighting and display, transistor, radio frequency identification (RFID) tag, superconducting, and biological applications. One current limiting factor in the use of organic materials for FHE applications beyond displays is the charge carrier mobility of organic semiconductors, which is still low when compared to that of amorphous silicon and worse yet when compared to polycrystalline silicon. [27]

Figure 1 shows a roadmap produced by the Organic and Printed Electronics Association (OE-A) for carrier mobility in organic semiconductor technologies. Additionally, the feature sizes and throughput (i.e., the area printed per unit time) that are possible via printing of electronic devices, which depend on the particular printing process, are also limited by printing equipment and ink technology, as shown in Figure 2. Both these concepts (charge carrier mobility and feature size versus throughput) are "important for the dimensional scaling of organic electronics, which could be of similar importance to the scaling of photolithography processes for silicon electronics, the driving force behind Moore's Law". [27]

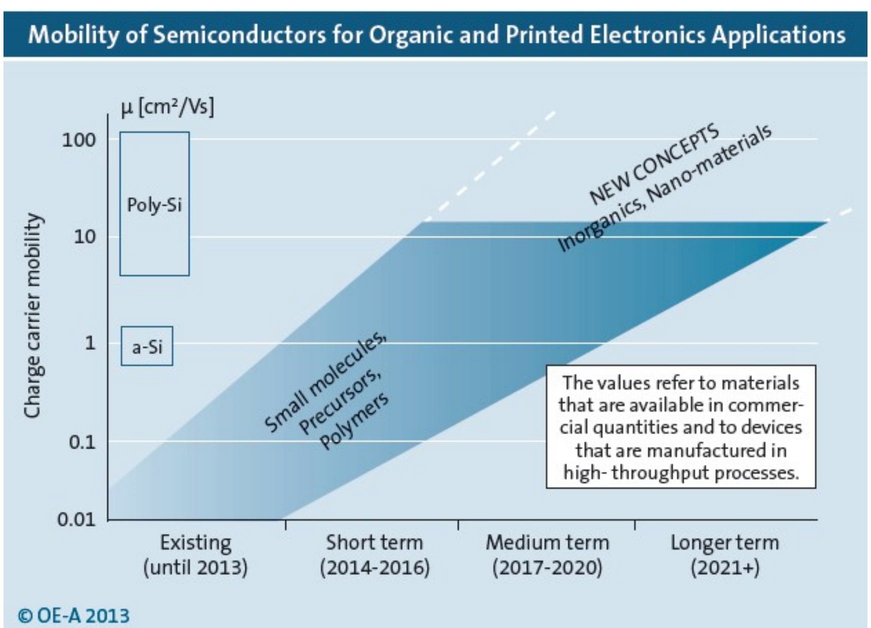


Figure 1. OE-A Roadmap for Charge Carrier Mobility of Organic Semiconductors (from [27])

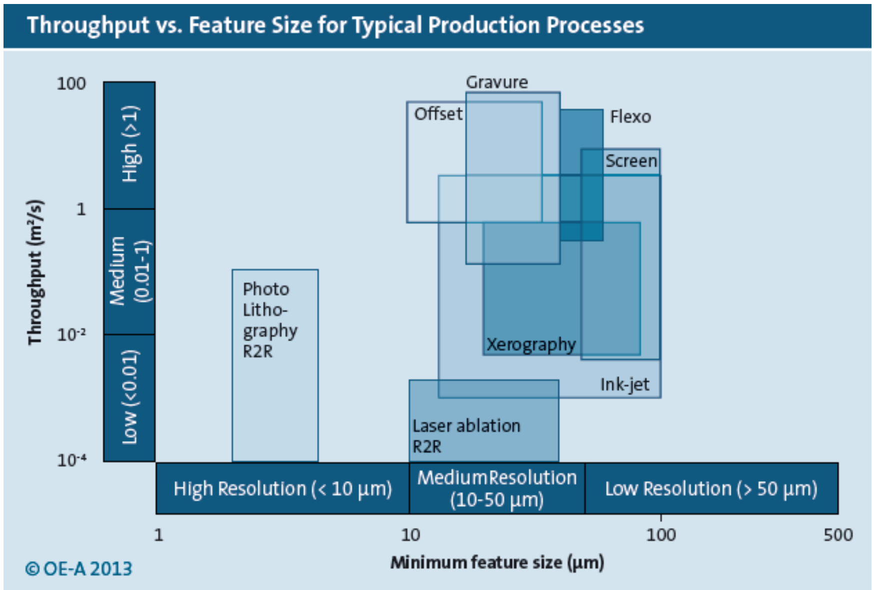


Figure 2. Throughput versus Feature Size for Typical (Organic Electronics Printing) Processes (from [27])

Three organic material technologies are heavily researched for FHE applications: polymeric materials, graphene, and CNTs. Each of these materials are discussed in detail in the various ink descriptions in Section 3.3, but they are also briefly described below to provide an introduction to the different materials.

3.2.1 Polymeric Materials

Polymers have long been used in electronics applications as structural materials and electrical insulators, and they continue to perform those same functions today. [28] Previously, if it was desired to make polymers have conductive properties, conductive fillers, such as silver, would have been added to the polymer formulation to increase its electrical conductivity. [29] However, it was discovered in the 1970s that some polymers could actually be made to conduct electric current. [30] In the last 20 years, major developments in synthetic polymer technology have allowed for electrical conductivity to be a valued and attainable property in certain polymers. [29] Today, not only can polymers have a structural and insulating function, but they can be conductive and semiconductive, and they can even be used to create transistors and ICs that are solely based on polymeric materials. [30]

The key advantages of polymers are that they are easy to shape and process, and their properties can be tuned by modifying their structures or processing. [28] They can be applied through simple and inexpensive techniques, such as printing and other roll-to-roll manufacturing methods, and they could enable mechanically flexible electronic components. Unfortunately, the conductivity and mobility of charge carriers in polymers is limited. They are incomparable to metals such as silver or inorganic semiconductors such as silicon, but can still be used in a wide variety of applications that utilize their advantages over conventional inorganic materials. [30]Today, polymers can be used as structural materials and electrical insulators in countless electronics applications. The areas where polymers can be used as semiconductive and conductive materials are not as broad, but some applications have emerged as ideal for polymer

electronics. [28] These applications include displays and light-emitting diodes because a semiconducting polymer emits light when a voltage is applied to it. Other application areas include polymer transistors and solar cells because enhanced mechanical flexibility would be an advantage in these areas. In time, more applications will emerge where polymeric materials will have an advantage. As future advances are made, scientists should have a deeper understanding of how the properties of these materials relate to their structure, and this should hopefully lead to the possibility of polymeric materials being designed with specific, desired electrical properties. [28]Further information regarding polymeric conductors, semiconductors, and insulators can be found in Section 3.3.3.1.1.5, Section 3.3.4.1.2, Section 3.3.6, and Section 3.3.7.

3.2.2 Graphene

Graphene is a two-dimensional (2D) material that at the atomic scale has a honeycomb lattice of carbon atoms. It is a very thin and nearly transparent one atom thick sheet. Its excellent physical properties make it a strong material with a low weight, and it conducts heat and electricity with great efficiency. [31][32] These properties make it a promising material for emerging and existing applications in printed & flexible circuitry, ultrafast transistors, touch screens, advanced batteries and supercapacitors, ultrafast lasers, photodetectors, and many other non-electronic applications. This 2-D layer of carbon atoms is a promising material for future electronics devices, but the graphene electronic device industry requires maturity and further development. Although this technology is in its infancy, remarkable progress has been made by the research community. Even though there are no graphene-based electronic devices in mass production, several companies already offer commercial graphene materials. [33]

The graphene material market value in 2013 was about $11 million, represented principally by the demand for the R&D and prototyping. The graphene electronics market is expected to reach $150M by 2020, with an increased focus on R&D. [34] The biggest restraint is the absence of a band gap, which inhibits large scale application towards manufacturing for replacing current electronics. The application of this material into electronic devices is still evolving, and it is not expected to move into the manufacturing industry in the near future. According to the market research report by Yole Development, in 2024 the graphene material market will be represented mainly by the demand for transparent conductive electrodes, advanced batteries, and supercapacitors. [35]

Some of the applications of graphene as electronics devices being investigated are:

- Field effect devices
- Radio frequency (RF) devices
- Electromechanical resonators
- Photosensors
- Flexible electronics
- Optical modulator

The University of Michigan has tuned the optical capabilities of graphene for future military applications to create infrared (IR) contact lenses. In a paper published in Nature

Nanotechnology, the research team measured how the light-induced electrical charges on top of a layer of graphene affected a current running through a bottom layer of the material separated from the first by an insulating barrier. [36] Researchers demonstrated an ultra-broadband photodetector design based on a graphene double-layer heterostructure. The devices demonstrated room-temperature photodetection from the visible to the mid-IR range, with mid-IR responsivity higher than 1 A/W.

In 2011 IBM research demonstrated in a proof of concept the development of a graphene IC with a broadband frequency mixer up to 10GHz. This IC consisted of a graphene transistor and a pair of inductors compactly integrated on a SiC wafer. The graphene transistor performance was inevitably degraded due to the harsh fabrication processes, but this was still a major milestone for the Carbon Electronics for RF Applications (CERA) program, funded by Defense Advanced Research Projects Agency (DARPA). [37] The gate length of the transistor was 240 nm with a RF of 100 GHz. The goal through the CERA program is to increase the transistor speed up to 1 THz. Recently, the IBM team changed their previous approach and reversed the conventional silicon IC fabrication flow, leaving graphene transistors as the last step of IC fabrication. This allowed for the preservation of graphene device performance, resulting in the first time that graphene devices and circuits could perform modern wireless communication functions comparable to silicon technology. The multi-stage graphene RF receiver IC consists of three graphene transistors, four inductors, two capacitors, and two resistors. All circuit components are fully integrated into a 0.6 mm2 area and fabricated in a 200 mm silicon production line, demonstrating unprecedented graphene circuit complexity and high silicon CMOS process compatibility. [38][39]

A new study reveals a high-quality continuous graphene oxide (GO) thin film that has the potential for ultrafast telecommunications. The non-linear response of the GO film can be tuned dynamically by varying the laser input. The research team developed a new processing method using a laser to create microstructures on the GO film. The fabrication and laser writing of this photonic material is scalable and low cost, compared with current manufacturing methods in semiconductor labs that requires a clean room for fabricating photonics chips. [40]The U.S. Army Research Laboratory’s (ARL) Sensors and Electron Devices Directorate (SEDD) is the principal Army organization for basic and applied research in sensors, electron devices, and power and energy to ensure U.S. military superiority. [41] The team has been investigating the use of graphene-based technology for use in low-cost IR imaging applications for the military. The long-term goal is to license and mass produce the technology for low-cost IR cameras. The following sections discuss the potential for the use of graphene materials in bio-sensor and radio frequency device applications.

3.2.2.1 Bio-Sensors

BlueVine Graphene Industries has developed a state-of-the-art patented system that allows for scaled-up graphene production with large-scale manufacturing capabilities. [42] With their scale-up technology, the company is making and testing bio-sensors and supercapacitors, with the hopes that their graphene glucose monitoring technology could replace current traditional testing systems at a much lower cost. A partnership between the Nanoscale Science and Engineering (CNSE) Center at State University of New York (SUNY) Polytechnic Institute and Graphene Frontiers, LLC will establish fabrication processes for the production of graphene biosensors.

[43] A dedicated graphene growth and transfer production line for wafer scale graphene will be established. Each of Graphene Frontier's Six Sensors biosensors consist of a field effect transistor (FET) with a graphene channel, which can be applicable for sensing diseases with multiple markers. [44]

3.2.2.2 Radio Frequency (RF) Device

IBM has been developing graphene-based receiver chips through a method where the graphene is added during the final manufacturing stages. While the chip was tested at a rate of 20 Mbps, due to limitation with the testing equipment and not the graphene-receiver itself, the receiver was able to process a digital transmission on a 4.3GHz RF. [45] A graphene RF transmitter was developed by researchers from Columbia University in New York and Yonsei University in Korea that could be easier to integrate onto chips. The 2-4 µm long strip of graphene was suspended above a metal electrode to create a graphene device that was able to generate a frequency-modulated electromagnetic signal, transmitting an RF signal at 100 MHz (in the middle of the frequency modulation (FM) spectrum). [46] Additional information on graphene can be found in Section 3.3.3 and Section 3.3.4.

3.2.3 Carbon Nanotubes

CNTs are essentially sheets of graphene rolled up into hollow cylindrical tube structures. CNTs exhibit extraordinary electrical properties and have a significant potential in electrical and electronic device applications, such as photovoltaics (PVs), sensors, semiconductor devices, conductors, energy conversion/storage devices, etc.

According to IBM, chips with nanotube transistors should be available commercially and mass produced after 2020. [47] These transistors must have features as small as 5 nm to keep up with the continuous miniaturization of computer chips by 2020. In 1998, IBM researchers made one of the first working CNT transistors, and after more than a decade, IBM was the first company to commit to commercializing this technology. IBM has made chips with 10,000 nanotube transistors, and the next goal is to create a transistor design that could be built with industry silicon wafers using existing manufacturing methods. IBM's design uses six nanotubes lined up in parallel to make a single transistor. Each nanotube is 1.4 nm wide, about 30 nm long, and spaced roughly 8 nm apart from each other. Both ends of the tubes are embedded into electrodes that supply current, leaving approximately 10 nm of their length exposed in the middle. A third electrode runs perpendicularly underneath this exposed length of the tubes and switches the transistor on and off to represent digital 1s and 0s.

Despite all of this research, IBM's nanotube effort remains within R&D, not in its semiconductor business unit. If the nanotube transistors are not ready soon after 2020 when the industry needs them, the window of opportunity might be closed. A team of Stanford University engineers was able to build a basic computer in 2013 using CNTs, which performed tasks such as counting and number sorting. [48] A basic operating system was also run by the CNT computer. The entire CNT computer is fabricated completely within a die on a single wafer. Each die contains five CNT computers, and each wafer contains 197 dies. However, limitations exist with this technology. CNTs are either semiconducting or metallic, and controlling this property is still unresolved. Also, tube alignment will have to be addressed before scaling-up the device in future manufacturing processes.

3.2.3.1 Memory Devices

CNTs have been used to create an alternative memory chip called NRAM®, pioneered by Nantero, Inc. [49] This CNT-based memory chip is as fast as and denser than dynamic random access memory (DRAM), and is expected to replace flash memory and/or DRAM in the future. This technology is highly resistant to environmental forces, including heat, cold, magnetism, radiation, and vibration. It is also compatible with existing CMOS fabs without the need for new tools and processes, and can be fabricated at a low cost. Scalable down to 5 nm, NRAM can be used in mobile computing, wearables, consumer electronics, space and military applications, enterprise systems, automobiles, the Internet of Things (IoT), and industrial markets. [50] Additional information regarding NRAM can be found in Section 7.0.

3.2.3.2 Flexible Electronics

Researchers from Korea and the Louisiana State University Agriculture Center have combined CNTs with paper in a novel battery design to produce a flexible device that can discharge energy much faster than traditional batteries. [51] This flexible battery is made of two sheets of paper, one acting as the cathode and the other as the anode. The paper is made of nanofibers of cellulose and backed with CNTs electrodes tangled with lithium-based materials. Another application of CNTs in flexible devices is for sensing and detecting bio-chemical agents. In a new study, researchers from Korea developed an all-carbon electronic device that is composed of CNT channels and graphite electrodes. [52] This all-carbon electronic device includes transistors, electrodes, interconnects, and sensors, and can be attached to a wide variety of surfaces, such as plants, insect, papers, clothes, and human skin via the van der Waals force.

3.3 Inks for Flexible Hybrid Electronics

The future of printed electronics depends heavily on the inks used to print the electronics devices. As new ink materials continue to be researched and developed, the capabilities enabled by ink technology will allow for a range of applications not achievable with conventional electronics manufacturing. Inks for printed electronics, sometimes referred to as functional inks, can be defined as materials deposited through various methods, including coating, printing, and deposition, that impart a specific electrical functionality and contribute to the creation of an electrical device. [53, 54]Several different types of inks are used to print electronics, including conductive, dielectric, semiconducting, resistive, electroluminescent (EL), and magnetic. Each of these will be discussed below, following a description of the requirements ink formulations need to meet and the broad categories inks fall into. [55]

3.3.1 Requirements for Ink Formulations

Traditional graphics printing methods have a variety of requirements, which are dependent on characteristics of the ink, substrate, and printing method. [56] First of all, the ink needs to have a viscosity that is appropriate for the particular printing method being used. Some techniques require very low ink viscosities, while others need the inks to have a thick, paste-like consistency. (Oftentimes, formulations with high viscosities will be referred to as pastes instead of inks.) The rheology, or flow characteristics, of the ink needs to be kept in mind since some inks demonstrate shear thinning behavior, where the viscosity decreases as a shear force is applied, such as the forces needed to push a fluid through a nozzle. The ink needs to have acceptable storage stability to ensure it will not oxidize over time, and dispersion stability so that aggregates do not form.

Viscosity, rheology, and stability will all play a role in the overall printability and performance of the ink. As the ink is applied, it needs to be compatible with the substrate, which is dependent on the chemistry of both the ink and the substrate surface. [56] The surface tension of the ink and the surface energy of the substrate dictate how well the ink will wet the surface and adhere to the substrate. Inks with a high surface tension will tend to form spherical droplets on a surface whereas inks with lower surface tension will spread out and wet a larger portion of the surface. Similarly, if a substrate has a high surface energy, the ink will be more likely to spread out rather than create spherical droplets that simply sit on the surface. In order to have acceptable wettability, the surface tension of the ink needs to be low enough and the surface energy of the substrate needs to be high enough to allow adequate spreading. However, a delicate balance is needed. If the wettability is too high, the ink may spread into an unintended area. Wettability is also dependent on the surface mechanics of the substrate, including roughness and porosity. The surface could have hills or valleys that prohibit the ink from spreading out and wetting a desired area of the substrate, or the substrate could be made of a material that causes the ink to penetrate beneath the surface before it is able to spread the desired distance. The ink also needs to have an appropriate drying efficiency for the printing method and intended application. [56] If the ink being applied is the first layer of many that will be needed to create a printed electronics component, the ink needs to dry quickly so it does not slow down the production process.

However, the ink cannot dry too quickly and cause problems with the printing equipment, such as nozzle clogging.

Liquid/solid interactions in the ink need to be taken into account as they define the line width and adhesion and can also give rise to segregation of the solute at the edge of the printed drop or line, a phenomenon referred to as the coffee stain effect. [57] The coffee stain effect describes the tendency of particulates suspended in coffee to move towards the edges of a coffee spill, causing a ring-like stain after the solvent has evaporated. This tendency causes an uneven distribution of particles within a droplet, which is problematic if an even distribution is necessary for a desired function. Therefore, research has been conducted in order to find ways to control or avoid the coffee stain effect. These ways include altering the ink formulation, changing the drying conditions, or depinning, which involves increasing the substrate contact angles (however doing so also leads to thick features and unstable printing conditions). The ink and substrate characteristics described above, in combination with the specific printing process being used, will dictate the resolution and quality of the printed product. Table 3 provides a summary of the requirements that need to be considered for ink formulating and printing.

Table 3. Important Factors to Consider When Formulating & Printing Inks

Factors	Definition	Why does it matter?
Viscosity	A fluid's resistance to flow [58]	The viscosity needs to be appropriate for the particular printing method in order to have the most efficient deposition of ink.
Rheology	The study of the flow of matter [59]	The flow characteristics of a material can change depending on the external forces being exerted upon it. It is important to know, for example, how an ink may react to being pushed through a nozzle or printhead.
Surface tension	The ability of a liquid to resist external forces due to the cohesive forces between molecules in the liquid [60]	The surface tension of an ink will affect its ability to spread out and adhere to the surface of a substrate.
Surface energy	Excess energy of the atoms at the surface of a material [61]	The surface energy of a substrate will affect an ink's ability to spread out and adhere to the substrate surface.
Wettability	The tendency of a liquid to spread out and maintain contact with a solid surface [62]	Dependent on both the surface tension of the ink and the surface energy of the substrate, wettability will dictate the interaction between the ink and the surface and define how the ink will spread out and adhere.
Drying efficiency	The efficiency at which liquid carrier is removed from the ink allowing the ink to harden [56]	Ink drying efficiency will affect the manufacturing of printed electronics devices. Inks need to dry quickly so that another layer can be applied, but they cannot dry so fast that they clog the application equipment.
Ink stability	The ability of the ink to resist changes that would move it away from a desired state [63]	Stability against aggregation will allow the ink to be easily processed and have a longer storage life. Stability against oxidation will prevent deterioration of the designed functions of the ink.

No matter what type of ink is being used, it is subject to the requirements described above, where characteristics such as surface energy, surface tension, and viscosity need to be tailored to the specific ink, substrate and printing process of interest. However, inks for printed electronics have an additional functional requirement that is dependent on their specific application, such as providing electrical conductivity along the printed pattern. [64] Functional inks have very similar compositions to conventional graphics inks, but with additional components that enable the desired electrical functionality. Detailed descriptions of the various types of inks used for printed electronics can be found below, including a discussion of the additives that can be included in printed electronics ink formulations and methods used to manufacture inks. After inks are deposited on the substrate of choice, they need to be treated in order to have the most optimal

performance. Post-treatment encompasses techniques for drying the inks in addition to methods that enhance the electrical functionality. These finishing methods are described in more detail in Post-Processing Methods, Section 4.1.3.

3.3.2 Types of Ink Formulations

Inks can be categorized into three broad categories: aqueous, solvent-based, and ultraviolet (UV) cured. [65] Each type has pros and cons, and all are used to some extent in the printed electronics industry. The main difference between the three types is the liquid carrier used in each formulation. Aqueous inks have water as their liquid carrier, while solvent-based inks use organic solvents. UV-curable inks contain little to no liquid carrier and are sometimes 100 percent solids formulations. Aqueous inks are environmentally friendly and safer for the end-user, but they require a large amount of energy to drive off the liquid carrier after the ink is applied. [65] Solvent-based inks are generally less expensive, more durable, and require less energy to evaporate the solvent, but through doing so harmful volatile organic compound (VOC) emissions are released into the environment. UV inks are cured through exposure to UV-light and can be applied to a wide range of substrates. [65] UV inks have the advantage of curing very rapidly, depending on the intensity of the light source, and can be used with high-speed production lines since the need to stop production for large drying units is eliminated. [66] Also, because they are normally a 100 percent solids formulation, UV inks do not release any harmful VOCs into the environment, nor do they require long drying times to evaporate water. However, they can be more expensive, require costly curing equipment, and tend to form brittle ink films. The type of ink chosen will depend on the intended application of the printed electronic device, availability of funds and capabilities, and environmental restrictions. Additionally, the type of ink chosen will depend on the desired substrate. Inks can be printed onto both rigid and flexible substrates to create printed electronics products. [67] However, the inks used in these two different applications are not always interchangeable. Since UV inks are 100 percent solids, the viscosity of these inks tends to be slightly higher, leading to thicker coatings on the substrate. [68] Thicker coatings can be brittle, which makes UV inks less applicable for flexible applications and more commonly used with rigid substrates. As new technology is developed, UV inks are increasingly used for flexible or hybrid applications, but they are not typically considered for challenging applications, such as the curved surfaces of vehicles. [65, 69] Solvent-based inks on the other hand are almost exclusively used with flexible substrates. [70]

Aqueous-based inks, while not used as often because they can require special surface coatings on the substrate [71], can be used in both flexible and rigid applications. [67]

3.3.3 Conductive Inks

Conductive inks are a key component of any printed electronics system, as they provide the conductive functionality for the product. The growth of the printed electronics industry relies heavily on new technology developments in conductive inks. The conductive ink and paste business was predicted to generate $1.6 billion in revenue in 2014. [72] With the increasing demand for efficiency and miniaturization in consumer electronics, this market is anticipated to more than double to reach $3.7 billion by 2018. [73] A very diverse range of products and compositions make up the conductive ink market, with the conductive components ranging from organic to inorganic materials. These conductive inks need to satisfy the general requirements of a printed electronics ink mentioned above, with the added requirement of electrical conductivity.

[64] The following sections will discuss the main components of a conductive ink composition, with specific focus on the various types of conductive materials that can be incorporated into the formulations.

3.3.3.1 Ink Composition

Conductive inks comprise a liquid carrier with dissolved and/or dispersed components. [64] The liquid carrier determines the basic fluid properties of the ink while the dissolved/dispersed components impart specific desired functionalities. The liquid carrier is typically water or an organic solvent, depending on the application. The dissolved/dispersed components include the conductive materials that give the ink its conductive capabilities, along with additives that have a variety of functions. The different types of conductive components that can be used in a conductive formulation are described in detail below. However, simply incorporating a conductive component into the formulation does not automatically result in a continuously conductive species. The ink has to be cured in order to enhance the conductivity, and the type of curing is dependent on the components present in the formulation. Metal nanomaterials need to be sintered in order to increase their conductivity, while conductive polymers might need to be cured through heat or photonic methods. The liquid carrier in the formulation will need to be removed by a curing process. The methods by which all of these are carried out are explained in Post-Processing Methods, Section 4.1.3. Removal of the solvent is what causes the conductive component to pack closely together. [74] Because of this, most conductive inks cannot be UV formulations because they do not allow for the necessary level of packing during their curing stage. Additives that are typically included in a conductive ink composition can include a binder, which holds all of the ink components together and helps it adhere to the surface of the substrate; aggregation protectants, which help to eliminate clustering of particles within the composition; and oxidation preventers, which reduce the risk of property deterioration caused by environmental exposure. These additives, as well as several others, are discussed in detail in Additives for Functional Ink Compositions, Section 3.3.10.

3.3.3.1.1 Conductive Component

The most important ingredient in a conductive ink formulation is the conductive component. Traditionally, conductivity is incorporated into the formulation through metals, but polymers and carbon-based structures are becoming popular as well. [72] Metals that are used to introduce electrical conductivity into printed ink formulations can be in many forms, including nanoparticles, flakes, nanowires (NWs), or complexes. Organic materials, such as polymers, CNTs and graphene, are being researched as an alternative to inorganic metals because they offer a variety of advantages, including potentially being more compatible with the organic substrates often used for printed electronics. Countless examples of all of these materials (metals, polymers, carbon) being used for FHE applications can be found in literature [75-82], and several of them will be referenced below in their respective sections.

3.3.3.1.1.1 Metal Nanoparticles

Metal nanoparticles used in conductive printed ink formulations can be made from a variety of metals such as silver, gold, copper, aluminum, nickel, tin, zinc, and platinum [83] but, silver is most commonly used followed closely by copper, gold, and aluminum. [64] Despite its high cost, silver is the material of choice for printed electronics applications because of its high bulk conductivity, the conductivity of its oxide layer, and its manufacturability. [84, 85] Copper

oxidizes easily, and unlike silver, its oxide layer is not conductive, so copper alloys are sometimes used in the place of pure copper to attempt to combat this issue. [74] While platinum is an extremely expensive metal (platinum – 1,134.25 USD/t oz., silver – 16.91 USD/t oz. [86]), it is often needed in extreme temperature situations where other metals are not adequate, such as in high temperature sensing, and also in lower temperature environments to reduce solder leaching and for blood analyte sensing capabilities. [74] It can be observed in the printed electronics industry that manufacturers have a few modes for producing these conductive materials and inks.

Some companies only produce metal particles and then sell their products to ink manufacturers. For example, NovaCentrix (Table 12, item 30), a company based in Texas, manufactures both silver and aluminum nanoparticles, but does not produce inks. [87] Applied Nanotech Holdings, Inc. (Table 12, item 31) offers silver nanoparticles, along with some nanoparticles which are not as commonly used for conductive inks including iron, nickel, and cobalt (these metals are typically used for magnetic applications, catalysts, and propellants). [88] Another option is for the company to produce nanoparticles and then formulate inks using their own nanoparticles.

Inkron (Table 12, item 62), a nano-technology company headquartered in Hong Kong, produces and sells both silver nanoparticles and nanosilver inks. [89] Other businesses import nanoparticles from an outside source to manufacture inks. Allied Photochemical (Table 12, item 6), headquartered in Michigan [90], obtains metallic nanoparticles from Degussa Corporation (Table 12, item 63) in New Jersey (part of German company Evonik Industries). [91, 92] Table 4 includes a large number of companies that are invested in metallic nanomaterials (including flakes, NWs, and complexes which will be discussed below) for the printed electronics industry, and despite the higher cost, a majority of them are primarily focused on silver.

Table 4. Companies Producing Metal-Based Nanomaterials for Conductive Inks

Company	Product	Metals
Nanograde (Table 12, item 64)	Nanoparticles, Nanoparticle inks	Al, Zn
Applied Nanotech Holdings, Inc. (Table 12, item 31)	Nanoparticles, Nanoparticle inks	Ag, Cu, Al, Ni, Fe, Co
NovaCentrix (Table 12, item 30)	Nanoparticles	Ag, Al
Johnson Matthey (Table 12, item 36)	Nanoparticles, Flakes, Flake inks	Ag
Inkron (Table 12, item 62)	Nanoparticles, Nanoparticle inks, Paste	Ag, Cu
Agfa-Gevaert (Table 12, item 3)	Nanoparticle inks	Ag
Allied Photochemical (Table 12, item 6)	Nanoparticle inks	Ag
Methode Electronics (Table 12, item 21)	Nanoparticle inks	Ag
Taiyo America (Table 12, item 44)	Paste	Ag
ULVAC (Table 12, item 24)	Nanoparticle inks	Ag, Au
Intrinsiq (Table 12, item 17)	Nanoparticle inks, Paste	Cu, Ni
PChem Associates (Table 12, item 34)	Nanoparticle inks	Ag
Ercon (Table 12, item 22)	Flake inks	Ag
PV Nanocell (Table 12, item 65)	Nanoparticle inks	Ag, Cu
Cambrios (Table 12, item 18)	NW inks	Ag
Genes' Ink (Table 12, item 66)	Nanoparticle inks	Ag
Seashell Technology (Table 12, item 19)	NWs, Nanospheres	Ag, Au
Kunshan Hisense Electronics Co. (Table 12, item 67)	Nanoparticle inks	Ag
Sigma-Aldrich (Table 12, item 42)	NWs	Ag, Al, Au, Ni, Zn, Ti
InkTec (Table 12, item 68)	Metal complexes	Ag
Gwent Electronic Materials (GEM) Ltd. (Table 12, item 46)	Metal complexes	Ag

3.3.3.1.1.2. Metal Flakes

Metal flakes can be used instead of nanoparticles as another way to incorporate conductivity into an ink formulation. Most often, this will be carried out in the form of silver or copper flakes. [54] Metal flakes can range in size from nano- to micro-scale, and they are sometimes preferred because their geometry can allow for increased surface area and therefore greater contact between the flakes as compared to particles. Additionally, sometimes the performance that results from three layers of nanoparticle ink can be achieved with one layer of flake ink. [74] Johnson Matthey (Table 12, item 36) produces and sells silver flakes and silver flake ink formulations that are optimized for screen printing methods. [93] These materials, which are compatible with a wide range of substrates, can be used for RFI shielding, membrane keyboards, flexible circuits, and flexible heaters. Additionally, DuPont offers a silver conductor called DuPont 5000 that is based on silver flake technology. [94] This material, which has been around for a considerable time, is used to create low-voltage circuitry, specifically on flexible substrates. DuPont has also recently released a new line of conductive materials for printed electronics, targeted specifically for membrane touch switch and smart card/RFID applications. [95] These

materials contain significantly less silver, and consequently are lower cost, but some of them can still achieve resistivity values comparable to their high-silver-containing counterparts.

For example, standard material DuPont 5029 contains <81% silver and has a resistivity of <8 mΩ/sq/25µm while new material PE815 (intended for smart card/RFID applications) contains <28% silver but has a resistivity of <10 mΩ/sq/25µm. Processing is what makes these results possible. The resistivity values were obtained after the two sheets of printed material were laminated at 80 °C. Lamination allows for the metal flakes and particles in the formulation to become essentially one large sheet of metal, resulting in extremely high conductivity values for the amount of silver contained. However, these new materials do have downsides as well. Many of these new materials do not demonstrate the mechanical flexibility that the standard conductive materials do and therefore would not be as applicable for flexible electronics applications. Some are also not as stable in high heat and high humidity conditions. All of DuPont's conductive materials, both standard and new, have trade-offs with regards to cost, resistivity, viscosity, hardness, stability, and flexibility, and the material used will depend on the particular application of interest.

3.3.3.1.1.3 Metal Nanowires

NWs can also be used as a way to introduce conductivity into a printed ink. Like with most other conductive components for inks, silver is the most commonly used metal for NWs, but other options exist. [72] One common advantage of metal NWs is the ability to have similar conductivity values at lower fill volumes as compared to nanoparticles, due to the high aspect ratio. [96] This could lead to decreased costs for compositions created from metal NWs. However, metal NWs sometimes have trouble regarding long-term operating stability [97] and cost-efficient high volume manufacturing [96]. Sigma-Aldrich (Table 12, item 42) offers a variety of NWs that have applications in electronics, including aluminum oxide, gold, nickel(II) oxide, silver, titanium(IV) oxide, and zinc oxide NWs [98] ((II) and (IV) refer to the oxidation state, or charge, of the metal ion [99]).

Seashell Technology (Table 12, item 19) [100], a nanomaterials company headquartered in California that manufactures and sells room temperature sinterable silver NWs, has several past and current Small Business Innovation Research (SBIR) contracts with the government for their NW technology. Contract topics include conductive transparent materials for indium tin oxide (ITO) replacement, anti-icing systems on remotely piloted aircraft, and environmentally friendly electronics for micro-electrical packaging. [101] In March 2015, it was announced that BASF Corporation had acquired all of Seashell's technology, patents, and know-how for silver NWs. [102] This acquisition is intended to extend BASF's portfolio of solutions offered to the display industry and strengthen their recognition as a leader in the electronics materials industry. More information regarding metal NW compositions and their use as transparent conductors can be found Section 3.3.4.

3.3.3.1.1.4 Metal Complexes

Metal complexes, which are commonly used in the production of thin metallic films for the conventional semiconductor industry, can be used to create metal atoms through chemical transformation. [64] A metal complex consists of a central metal atom surrounded by bound ligands. [103] Ligands perform a variety of functions, including dictating the reactivity of the

metal atom as well as protecting it. Figure 3 shows more detail about the structure of metal complexes and the chemical process that transforms the complex into a metal atom. Metal complexes are sometimes preferred for ink formulations because the ligands help to protect the metal from oxidation and aggregation. Unfortunately, the chemical process required to transform the complex into the metal atom can be expensive and time-consuming.

The only examples of commercial metal complex-based inks are produced from organosilver compounds. Two companies that produce these materials are InkTec, which is based in Korea, and GEM, headquartered in the United Kingdom with an overseas office in San Francisco (Table 12, items 68 and 46, respectively). InkTec has several different inks that can be used with inkjet, gravure, slot die, flexography, screen, and knife coating/printing methods, and in addition to metal complex inks, they also offer nanoparticle and flake inks. GEM has various types of electronic materials, including electrode pastes, EL products, high speed printing pastes, dielectric pastes, and graphene materials. In Figure 3, A, B, C, and D represent various ways the metal (M), coordinating ligand (CL), and anionic ligand (AL) can be arranged. During a chemical transformation process, such as chemical vapor deposition (CVD), the complex decomposes cleanly into metal and byproducts, and the metal is deposited onto the substrate surface. The ligands, or byproducts, can be passive and simply stabilize the metal cation, or they can be active and undergo chemical transformation during the decomposition.

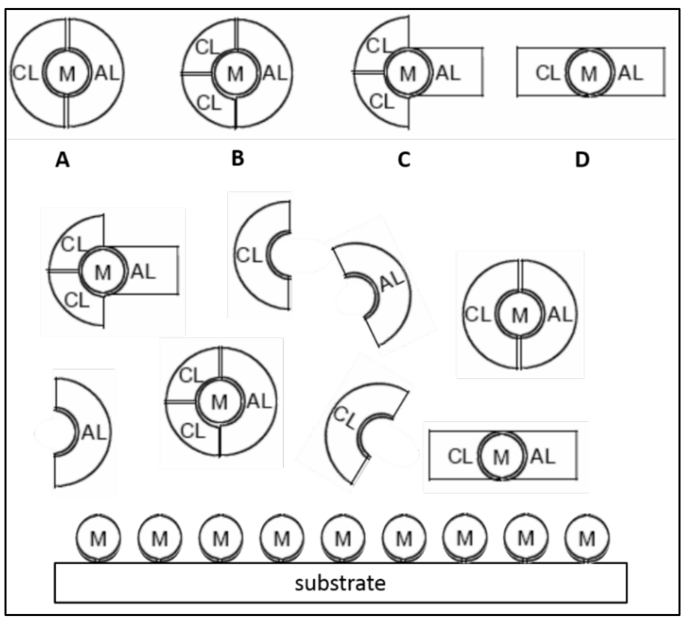


Figure 3. Various Arrangements of Material Components During Chemical Transformation [313]

3.3.3.1.1.5. Conductive Polymers

Organic materials, such as polymers, can also be used as the conductive component in conductive ink formulations. Typically, polymers are insulating materials, but a class of polymers exists that has conductivity levels between those of semiconductors and metals, and these materials can be used as conductors. [104] In 2000, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa won the Nobel Prize in Chemistry for "the discovery and development of conductive polymers". [105] This award recognized their discovery in the 1970s that polymers

can be made conductive via doping. By removing an electron from the polymer's conjugated π-orbitals, the electrons become delocalized along the polymer backbone and lead to electrical conductivity. The electrons or holes in the conjugated polymers move through two main mechanisms of charge transport: band transport and hopping. [20] Band transport occurs when the charge travels down the chain in the direction of the applied field. Band transport is also called travelling coherently, because the charge is moving down a conjugated (alternating single and double bonds) backbone. If the material is not conjugated, the only possible transport is hopping. Hopping is when charge carriers "jump" from one monomer to another, which are not necessarily located adjacent to each other.

The first generation of conductive polymers, which includes polyacetylene and polypyrrole, are not used as often today because they are not as suitable as the next generation of conductive polymers in terms of processability and long term conductivity stability. [104] Recent research has been focused on materials based on polyaniline and polythiophene. Heraeus (Table 12, item 47), under the trade name Clevios™, has developed what they deem as the latest generation of conductive polymers based on poly(3,4-ethylenedioxythiophene), or PEDOT. Because conjugated polymers tend to be semicrystalline and therefore stiff in nature, some of these conducting polymers are insoluble in common ink solvents, so companies often use chemical derivatives of conjugated polymers to increase solubility. [20] One of these companies is Agfa (Table 12, item 3), which has a line of Orgacon™ products (sold through Sigma-Aldrich). [106] These materials are derivatives of PEDOT and are based on poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), or PEDOT:PSS. These PEDOT:PSS-based products include conductive inks for screen printing and inkjet applications. Conductive polymer ink formulations are also extremely popular in the academic world, as researchers attempt to understand all of the important variables when formulating and printing these compositions.

Researchers at Western Michigan University have been studying the gravure printability of polyaniline and PEDOT:PSS, specifically with regards to surface tension and substrate wetting. [107] Through their studies, they have discovered that film quality is heavily dependent on the evaporation of solvents and in order to minimize defects, it is ideal if all solvent evaporates at the same rate. They also learned that it is very important to consider things like shear thinning and polymer swelling when formulating conductive polymer inks. A group of scientists from the University of Wollongong in Australia published a paper in 2012 describing their successful printing of PEDOT:PSS materials onto soft substrates such as silicone gum and polyethylene terephthalate (PET). [108] With their process, they were able to obtain structures down to 600 nm in width and 10 – 80 nm in height within patterned arrays. Previously, some of the same researchers from University of Wollongong demonstrated that aqueous polyaniline nanodispersion inks could be printed using a piezoelectric inkjet desktop printer. [109] Researchers from Stanford University have also investigated the stretchability of PEDOT:PSS films cast from aqueous suspensions of PEDOT:PSS for use as electrodes in transparent, capacitive pressure sensors for mechanically compliant optoelectronic devices. [79]

Inks made from organic polymers such as these are becoming increasingly popular compared to traditional metal-based conductive inks because of their potentially lower cost, ease of manufacture and processability, environmental stability, and other rapid advancements in recent

years, and they can be used in a variety of areas. Figure 4 demonstrates the potential applications for conductive polymers in the microelectronics industry.

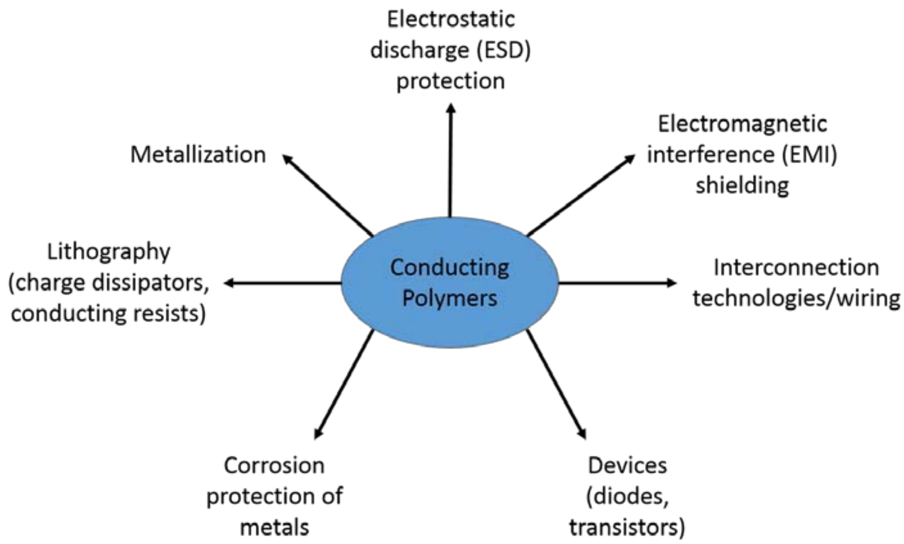


Figure 4. Applications for Conducting Polymers in the Microelectronics Field [110]

3.3.3.1.1.6. Carbon-Based Compositions

Carbon-based materials in the form of nanotubes and/or graphene, are becoming increasingly popular components for conductive inks in printed electronics applications. Metal-based conductive inks are expensive and require high-temperature curing, which limits the substrates that can be used. [111] While carbon-based inks typically have lower conductivities than silver-based inks, they are becoming desirable because of their cost, flexibility, processing, and because of the growing research around CNTs and graphene.

3.3.3.1.1.6.1. Carbon Nanotubes

CNTs are sheets of one-atom-thick carbon bonded together in a hexagonal pattern (graphene) that have been rolled into hollow cylindrical tube structures. [112, 113] The properties of CNTs, such as their electrical or mechanical behavior, are dictated by several variables including the orientation and angles of the rolled sheets and whether they are single- or multi-walled structures. For example, depending on their orientation, CNTs can display metallic or semiconducting characteristics. (The semiconducting form will be discussed in detail in Section 3.3.7). Additionally, CNTs can vary greatly in length, but the nanotube diameter is typically on the nanometer scale.

CNTs have outstanding optical and electrical properties, excellent strength and flexibility, and high thermal and chemical stability, but there are safety issues with them, and in the past they have been difficult to manufacture at a competitive cost. [114] SouthWest NanoTechnologies Inc. (SWeNT) (Table 12, item 29) produces selective single-walled carbon nanotubes (SWCNTs) through a patented CoNoCAT catalytic method that is based on research conducted by Professor Daniel Resasco (SWeNT's chief scientific officer) at the University of Oklahoma. This method allows for scalable production of SWCNTs with much better control and at affordable prices. [115]

Brewer Science develops CNT electronics materials for high-speed device sensors, printed electronics inks, and non-volatile memory devices. [116] Brewer Science's line of CNT inks for printed electronics are applicable with various printing methods, including aerosol jet, inkjet, screen, spray coating, and drawdown bar, and they are applicable as conductive traces in flexible conductors, RFID tag antennas, and others including recent developments such as batteries, transistors, etc. Much research has been invested into incorporating CNTs into inks for printed electronics applications. Companies and research organizations, including SWeNT, Aneeve Nanotechnologies [117], University of California at Berkeley [118], and Raymor-NanoIntegris (Table 12, item 55) [119] have progressed from making basic CNT inks to depositing high-performance CNT transistors on plastic substrates.

NanoIntegris was co-founded by Prof. Hersam from Northwestern University after publishing a breakthrough paper in Nature Nanotechnology describing a process to sort CNTs by electronic structure (metallic or semiconducting). The company scaled up production and lowered cost for developing high-performance nanomaterials that are used to accelerate industrial nanotube-based electronic devices, such as conductive films, thin-films transistors, PVs and sensors. Their materials have been used in various next generation electronics applications. IBM used their CNTs to create low-cost TFT devices. [120] TFT CNT sensors are unique since they respond to analyte surface coverage, as opposed to conventional sensors that respond to analyte concentration. A timeline describing some of the recent innovations in CNT technology for FHE is shown in Figure 5. More information about CNTs can be found in Section 3.3.4.

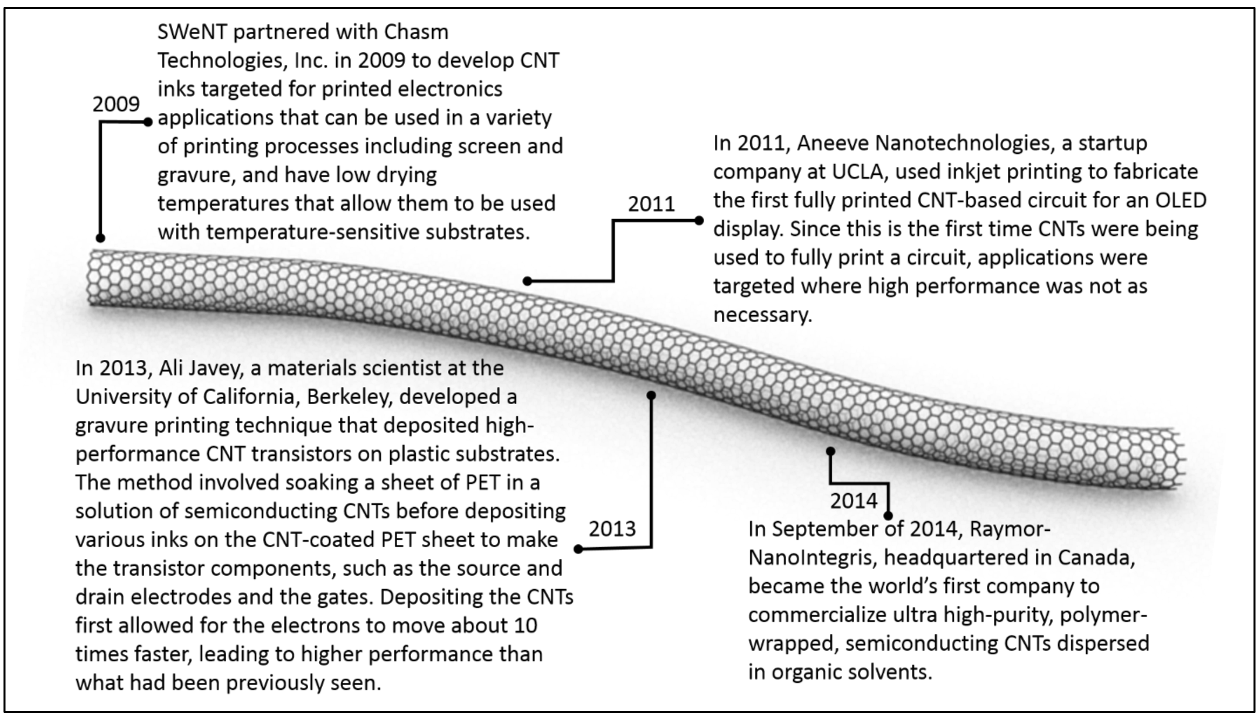


Figure 5. Timeline of Recent CNT Technological Achievements in Printed Electronics Industry [116-119, 121, 122]

3.3.3.2. Graphene

Despite the advances in CNT ink technology, work still needs to be performed to improve dispersion stability and processability. [111] Therefore, graphene-based inks have been heavily studied as an alternative in carbon-based conductive technology. Graphene is a one-atom-thick sheet of pure carbon atoms bonded together in a hexagonal pattern. [123] Essentially, graphene is the material that is rolled up to create CNTs, and because it requires less synthesis steps, graphene is easier to produce than CNTs. [20] Graphene was first isolated in 2004 at The University of Manchester in England [124], and therefore the graphene industry is still extremely new and volatile. Due to its structure, graphene is the thinnest, lightest, strongest, and most electrically conductive material known to man. [125] It also is the best conductor of heat at room temperature. However, it is very expensive and difficult to produce at high levels of purity, and due to its lack of band gap, it has been difficult to use for electronics applications. Much research has been done to address these downfalls.

As graphene has become a heavily researched technology for many different industries, including electronics, various ways to create or manufacture graphene have also been investigated. [57] One of the primary ways is through exfoliation, particularly mechanical exfoliation of graphite crystals, which creates high quality thin graphene flakes. Mechanical exfoliation of graphene was pioneered by Prof. Rodney S. Ruoff and coworkers at Washington University in 1999 using an atomic force microscope (AFM) tip to manipulate small pillars patterned into highly oriented pyrolytic graphite (HOPG) by plasma etching. Unfortunately, this particular exfoliation process is difficult to scale up. As a work-around to the scale-up issues, exfoliation methods that take place in solution have been developed. [57] These include exfoliating graphite in organic solution to obtain monolayer or few-layered graphene, and exfoliating GO in solution followed by a reduction process to produce low cost, large quantity, low quality graphene films.

The most significant advantages of solution-based methods of fabricating graphene films are low cost and massive scalability. One of the most important requirements for incorporating a solution-based technique into device fabrication is to obtain uniform and reproducible films. Vacuum filtration methods are usually used to achieve this, but the films can also be deposited through spray methods, electrostatic self-assembly, along with others. Other ways to produce graphene include growth methods. [57] Graphene can be grown on metal substrates through an epitaxial growth process, and this method is suitable for large scale production. Manufacturers can also use CVD to synthesize large area, high quality monolayer or few-layered graphene on copper or nickel substrates. If graphene is grown on metal through a CVD process, it often has to be transferred to a different substrate. This can be performed through various methods, including transfer printing, roll-to-roll thermal transfer methods, and processes that transfer onto a polymer support, among others. Graphene-based inks that enable printing onto substrates for FHE applications have been developed at Northwestern University. [126] The research team was able to spray layers with thicknesses of 14 nanometers, but for use in ink-jet printers, a graphene ink-powder form has to be developed that allows graphene to keep its attractive electrical properties, such as high conductivity. While the graphene-based ink leads to patterns that are 250 times as conductive as previous attempts to print graphene-based electronic patterns, the paper doesn't discuss whether the material can be engineered to act as a semiconductor.

Engineering a band gap into graphene remains a critical prerequisite for applying the material in electronics. [127] One of the pioneers in the graphene electronics industry is Vorbeck Materials (Table 12, item 23), headquartered in Jessup, MD. They have developed Vor-Ink™, a graphene-based line of conductive inks and coatings that offer high conductivity, flexibility, high-speed printing, and low-temperature curing. Their products can be utilized for screen, flexo, and gravure printing processes with specific applications in interfaces, RFID, packaging, wearable technology, and sensors/biosensors. [128] Additionally, Haydale (Table 12, item 69), a leader in facilitating the commercial application of graphene, partnered with GEM (Table 12, item 46) to develop graphene-based inks that can be used for light flexible displays, plastic electronics, printed circuit boards (PCBs), liquid crystal displays (LCD), thin film PVs, e-paper, sensors, and organic light emitting diodes (OLEDs). [129] The graphene market is expected to grow from approximately $20 million in 2014 to more than $390 million in 2024. [130] Seeing the future in graphene-based materials, several companies have invested in this industry, including Applied Nanotech Holdings, NanoIntegris, Graphene Technologies, and XG Sciences (Table 12, items 31, 55, 20, and 14, respectively). A list of companies that offer or are developing graphene products, with an accompanying short company history, can be found in Table 5.

Table 5. Companies Involved in Graphene Inks Market

Company	Headquarters	Brief History	Graphene Products	Other Products
NanoIntegris	Canada	Founded in 2007 as a spinoff of Northwestern University. Acquired in 2012 by Raymor Industries	Nanoplatelets	CNTs
Graphene Technologies	California	Founded in 2010 and still in development stages	Still in development stages for graphene materials (polymer systems, conductive coatings, nano-dielectric systems)	Mono-crystalline magnesium oxide as dielectric material
XG Sciences	Michigan	Founded in 2006. Technology based on manufacturing process developed at Michigan State University	Nanoplatelets, sheets, inks, coatings	N/A
GEM	United Kingdom	Founded in 1988 to provide manufacturing materials to the electronics industry	Ink (with partner Perpetuus Carbon Group Ltd.), other graphene materials under development	Pastes, inks, etc.
Vorbeck Materials	Maryland	Founded in 2006. Graphene material (of which Vorbeck has exclusive rights) developed at Princeton	Single sheet graphene, inks, coatings, rubber, flexible batteries	RFID tags, flexible battery straps
Haydale	South Wales	Formed in April 2010 to use a plasma process to functionalize carbon nanomaterials	Functionalized graphene nanoplatelets (GNP), graphene ink, functionalized graphene layers	Functionalized single & multi-wall CNTs
Applied Nanotech Holdings, Inc.	Texas	Founded in 1989 as Si Diamond Technology. Applied Nanotech was created as a subsidiary in 1996.	Graphene films	Conductive inks & pastes, nanomaterials
Graphenea	Spain (U.S. subsidiary in Massachusetts)	Founded in 2010 and is a partner of the Graphene Flagship, a 10- year investment push research program for graphene	Monolayer, bilayer, and trilayer graphene on various substrates, GO dispersion, GO film	N/A

The unique properties of graphene make it of interest for high-speed electronics, wireless devices, mass communication media, and telemedicine device applications. [57] In fact, several different applications have already be researched and some successful results have been reported. Graphene has been studied as an interconnect material for ICs because of its very high maximum current density, its ability to achieve line widths below 50 nm, and its stretchability. Graphene

electrodes are also highly researched, specifically for applications in flexible FETs, flexible organic photovoltaics (OPVs), OLEDs, transparent flexible touch screen panels, and stretchable transistors. More applications for graphene-based FHE are described in Section 3.2 and Section 7.0. As mentioned above, one of the current issues with graphene is its lack of an inherent band gap, which limits its uses for electronics applications. Therefore, efforts have been made to alter graphene so that it can function as a semiconducting material.

In April 2012, a press release announced that researchers at University of Wisconsin-Milwaukee had developed a new form of graphene, called graphene monoxide, through a chemical modification of graphene. [131] This new material is capable of acting as a semiconductor, and it can also be mass produced inexpensively. Graphene monoxide was discovered almost by accident – the researchers were trying to create multilayered graphene. Instead, they found that by heating GO under a vacuum, the material took on an aligned structure to create graphene monoxide. While this material could enable countless applications for graphene-based electronics, the research group's first goal is understanding the triggering mechanism for the realignment they observed.

A team from University of Exeter in the United Kingdom also developed a variation of graphene in April 2012 that allows graphene to be more compatible with electronics applications. [132] The new material consists of two layers of graphene sandwiching molecules of ferric chloride, which increases the electrical conductivity of graphene without compromising its transparency. They claim that their invention, which they are calling GraphExeter, is the "most transparent, lightweight, and flexible material ever for conducting electricity." While this might be a bold statement, the associated journal article abstract does mention that this material outperforms the current limit of transparent conductors, including ITO, CNT films, and doped graphene materials. While no specific applications have been identified for this material yet, they mentioned that it can be used for a range of industries, from PVs to wearable electronics and optoelectronic devices.

3.3.3.3 Material Property Comparison

Conductive materials are often defined by their conductivity, which is a measure of the ability of the material to conduct an electrical charge. [133] The electrical performance of the conductor increases as the conductivity of the material increases. Table 6 summarizes the conductivity values for common conductive materials, both inorganic and organic. Since some organic conductive polymer materials are typically doped to increase their conductivity, conductivity ranges are provided for those materials based on various experimental results found in literature.

Table 6. Conductivity Values for Common Conductive Materials

Material	Conductivity
Inorganic	
Silver	6.30 x 107 S/m [134]
Gold	4.10 x 107 S/m [134]
Copper	5.96 x 107 S/m [134]
Aluminum	3.50 x 107 S/m [134]
Nickle	1.43 x 107 S/m [134]
Tin	9.17 x 106 S/m [134]
Zinc	1.69 x 107 S/m [134]
Iron	1.00 x 107 S/m [134]
Cobalt	1.72 x 107 S/m [135]
Organic	
Polyacetylene	1.7 x 10-7 to 2.0 x 106 S/m [136] [137]
Polypyrrole	2.66 to 4.56 x 106 S/m [138]
Polyaniline	6.28 x 10-9 to 1.30 x 104 S/m [139] [140] [141]
Polythiophene	7.53 x 10-4 to 1.0 x 105 S/m [142] [143]
PEDOT	1.0 x 10-5 to 1.0 x 102 S/m [144] [145] [146]
PEDOT:PSS	7.82 x 10-1 to 1.0 x 105 S/m [147] [104]
CNT	106 to 107 S/m [148]
Graphene	1.00 x 108 S/m [134]

3.3.3.4. Recent Advances in Conductive Inks

Professor Jennifer A. Lewis, previously a professor at the University of Illinois at Urbana-Champaign and now the Hansjörg Wyss Professor of Biologically Inspired Engineering at Harvard School of Engineering and Applied Sciences, has been heavily involved in direct write (DW) assembly and three-dimensional (3D) printing for a majority of her career. [149] As printed electronics have become more of a reality, some of her research has shifted focus to include direct writing of functional and conductive materials. Additionally, she has been invested in developing alternative inks that solve some of the problems associated with today's functional inks, including the issue of nanoparticles clogging nozzles and high post-treatment temperatures not being compatible with temperature-sensitive substrates.

A paper was published in January 2012 that describes a reactive liquid silver ink developed by Professor Lewis and her research team at the University of Illinois at Urbana-Champaign. [150] This ink formulation contains silver acetate dissolved in aqueous ammonium hydroxide and can be printed through direct ink writing, inkjet, or airbrush spraying. Only after printing and evaporation do silver particles form from the silver acetate, allowing for printing nozzles as small as 100 nm to be used. The ink can be dried at room temperature (23° C) for 24 hours to achieve conductivities around 106 S/m or can be annealed at 90° C for 15 minutes to obtain the conductivity of bulk silver (6.25 x 107 S/m). When dried at room temperature, the presence of both silver and silver acetate were observed, but when dried at 90° C, only peaks for silver were

found using x-ray diffraction. After the slightly elevated temperature annealing process, the final silver loading reached 22 weight percent, which is comparable to other silver precursor-based inks. In addition to the high conductivity and the ability to print with extremely small nozzle sizes, this new technology is highly transparent and can be stable for months if stored in a sealed vial. [150] Unfortunately, because of its low viscosity, significant wetting is observed when printed, so feature sizes below 5 µm are yet to be achieved even though the ink is printed at a resolution of 100 nm.

A spin-off company, Electroninks Incorporated, was created in January 2013 from the research lab of Professor Lewis. [151] This company uses similar technology for their Circuit Scribe product as the liquid silver inks described above, and they are targeting direct writing techniques specifically through the use of rollerball pens. Electroninks promotes Circuit Scribe as a non-toxic, water-based, conductive silver ink for use in rollerball pens. The technology behind the Circuit Scribe product is described in an article from 2011 in Advanced Materials. [152] This paper describes the ink as an aqueous solution of silver nitrate that is reduced to produce a silver particle ink in the presence of poly(acrylic acid) (PAA) as the surface capping agent, and diethanolamine as the reducing agent. [152, 153] The components of the ink formulation are mixed together, which causes a reaction and the creation of silver nanoparticles of approximately 5 nm in diameter. The composition is then heated to 65° C for 1.5 hours in order to increase the diameter of the nanoparticles to approximately 400 ± 120 nm.

Circuit Scribe ink was designed specifically to be used in a rollerball pen on a paper substrate. [152] They explain that the benefits of printing conductive features using a pen and paper include portability, cost, and compatibility with various ink formulations. In order for an ink to perform efficiently in this application, it needs to readily flow out of the pen upon use but resist leaking, drying out, and coagulating. Circuit Scribe ink can flow through a pen with a ball diameter as small as 250 µm, can be stable for months in a sealed container, and can be used on both soft and rigid substrates. The conductivity of the inventive ink composition (approximately 2 x 107 S/m) is orders of magnitude higher than other silver nanoparticle inks available, perhaps due to the fact that the capping layer is removed after application or the particle size is increased. The Circuit Scribe ink is demonstrated in applications for electronic art, large area light emitting diode (LED) grids, conductive text, and 3D antennas. [152] This technology could lead to elimination of costly printing equipment, and could aid in the development of more viscous inks that would not permeate and wet out the substrate like the ones described above in. [150] However, currently, this product seems targeted for small scale applications, such as an educational classroom tool, as opposed to a product that would be used for high-speed industrial manufacturing of printed electronics components and devices. [154]

In the commercial sector, Henkel has been heavily researching conductive silver inks, and has recently released a new line of inks. [155] Henkel already has a line of printed electronic inks that included silver inks, carbon inks, dielectric inks, and other specialty inks, but their new line of printed silver inks have increased conductivity. The higher conductivity allows end users to consume less ink, have increased design flexibility, enable additive processing, and have more sustainable processes overall. Henkel's current commercial materials, Electrodag 725A and 479SS are standard materials for membrane switch applications and have sheet resistance values

ranging from 12 – 21 mΩ/sq at 25 μm. [155] In comparison, their three new materials have sheet resistance values ranging from 2.5 – 13 mΩ/sq at 25 μm.

The three new inks are designed to be used in different environments. One of the inks (ECI1010) is highly conductive (4 – 6 mΩ/sq at 25 μm) and is relatively stable after being subjected to mechanical deformation. The second ink (ECI1011) is even more conductive (2.5 – 2.8 mΩ/sq at 25 μm), but cannot handle as much mechanical stress. The third ink (ECI1012) has a slightly higher resistance (12 – 13 mΩ/sq at 25 μm), but is stable under folding mechanisms and offers a lower silver loading, making it a lower cost option. Because of their higher conductivity values, all three of these inks can have thinner track thicknesses and widths without negatively affecting performance, allowing them to be approximately 40 – 50% more cost efficient than traditional silver inks. Henkel's new line of conductive silver inks are designed to be screen printed, but they can also be used in slot die or flexo applications, and they are typically dried at approximately 150 °C. [155] These inks have acceptable flexibility values (except for ECI1011), good adhesion to PET and PI, and are reliable under high heat and/or high humidity conditions. One application these new inks can be used for is printed heaters, which will be discussed in Section 7.0.

3.3.3.5 Current Problems & Future Trends

As can be seen through the discussions above, the conductive ink market has many opportunities and directions moving forward. Some of the main markets for conductive inks involve PVs, displays, and sensors, and these areas are showing promise for growth in the near future. However, there are problems facing this market today, which revolve mainly around cost, performance, and processing. With silver being the most popular and commonly used metal for conductive ink formulations, and also unfortunately a very expensive metal, problems are going to arise regarding ink pricing. [156] Therefore, the future of conductive inks needs to involve attempts to reduce that cost, which can be achieved in a couple ways. Some ink producers, like Creative Materials (Table 12, item 12), have been developing inks that contain a lower percentage of silver while still maintaining the same level of conductivity.

Another option is to increase the quality and performance of the ink films so that less conductive material needs to be used. Ink developers are also looking at materials that could replace silver in ink compositions, such as copper. Intrinsiq Materials (Table 12, item 17) has already noticed an increased interest from its customers in copper-based inks. Another area for improvement in the conductive ink market is general ink performance. [156] Depending on the application, ink compositions need to have a variety of performance attributes, including conductivity, flexibility, and transparency. Being able to increase the conductivity of ink formulations, especially ones where organic conductors are used, would allow the formulations to have a larger stake in the market. When conductive ink formulations are used on flexible substrates, the formulation must exhibit mechanical flexibility. [157]

Oftentimes with today's conductive ink formulations, the ink is too brittle and as the substrate flexes, the ink cracks, destroying conductivity. As a result, future development in conductive inks, especially inks targeted for flexible applications, will need to focus on designing mechanical flexibility into formulations. Finally, some conductive ink formulations are being used to produce transparent conductive films (TCFs). [156] Therefore, working to increase the

transparency of ink formulations would greatly help this type of conductive ink become more prevalent in the market. The processing of inks, including printing and post-treatment methods, is an area where improvements could be made. [156]

There is a desire to predominantly use high-speed printing methods in order to have more efficient production capabilities. However, not all conductive inks are compatible with these high-speed processes, and work needs to be performed to address this issue. Another problem associated with conductive inks is the high sintering temperatures or long curing times required to make them conductive. Therefore, researchers are continually working to lower the curing/sintering temperature, decrease the curing time of the ink components, or resort to alternative post-treatment methods, which are discussed in Section 4.1.3. The future of conductive inks revolves around addressing any or all of these problems in order to provide a more cost effective and efficient conductive ink solution for the FHE industry. Table 7 provides a snapshot of the advantages and disadvantages of the various conductive technologies discussed above.

Table 7. Advantages & Disadvantages of Various Conductive Technologies

Conductive Component	Advantages	Disadvantages
Metals	• Extremely high conductivity • Existing technology	• Expensive • Susceptible to oxidation
Conductive polymers [158] [159]	• Processability • Tunable electrical properties • Mechanical flexibility • Lightweight • Low cost • Thermal & environmental stability	• Lower conductivity • Poor solubility in solvents • Lack of homogeneity & reproducibility
CNTs [160] [161]	• Tunable conductivity (can reach high levels) • Strong • Lightweight & mechanically flexible • Transparent	• Difficult to produce • Not readily available in nature • Only conduct electricity in one direction (along the length of the tube) • Safety hazards
Graphene [162]	• High conductivity • Abundant material • Transparent • High chemical resistivity • Strong • Lightweight & mechanically flexible	• Difficult to isolate & produce high purity materials • Expensive • New & relatively unknown material • Unknown potential safety hazards

3.3.4. Transparent Conductive Materials

Many electronic devices or components require the use of TCFs or coatings. These materials are optically transparent and electrically conductive in thin layers, and are used in devices such as displays, solar cells, and optoelectronics. [163] Traditionally, TCFs are created through vacuum

deposition of an inorganic material, most commonly ITO. [164] ITO is a solid solution of indium(III) oxide and tin(IV) oxide, and it is the most commonly used transparent conductive material because of its low resistivity values and high transmittance characteristics. However, since indium is an extremely rare metal, ITO is an expensive material. Additionally, ITO is not an excessively pliant material, so it is not ideal for flexible electronics applications. In an attempt to compensate for the high expense of ITO, alternative inorganic oxides have been considered for some transparent conductive applications. One material in particular is aluminum-doped zinc oxide (AZO). AZO has a lower cost and acceptable electrical and optical properties, but unfortunately it does fall short of ITO's performance in almost every area except cost. [164]

While some of these inorganic materials might be more mechanically flexible than others, inorganic transparent conductive materials in general are not suitable for flexible electronics applications. Efforts have been made to engineer flexibility into inorganic TCFs. In 2004, an article was published that described a method of sputtering thin films of ITO onto a polyester substrate designed for flexible display applications. [165] The ITO-coated materials were then investigated for the effects that mechanical stresses had on electrical performance of the material. It was observed that as the film's thickness decreased, it was more apt to flex without a significant negative impact on the device performance. However, as some flexible electronics applications require extreme mechanical adaptability, this technology is not an all-encompassing solution.

3.3.4.1. ITO Replacement Materials

With the disadvantages associated with ITO and similar inorganic TCFs, recent research has been focused on ITO replacement materials, especially as the size of displays continues to increase. The replacement materials that have been and are currently being researched can be grouped into five main categories: metal mesh, silver NW, conductive polymer, CNT, and graphene. [166] Graphene is the most researched ITO replacement, with CNT and metal mesh following closely behind. The five material categories are discussed briefly below.

3.3.4.1.1. Metal Mesh/Silver Nanowire

Using metal mesh or silver NWs in TCFs is a way to achieve mechanical flexibility without sacrificing too much conductivity. To create metal mesh, metal nanomaterials are arranged in a grid pattern through a printing or direct writing method. [167] As thin films, these metal grids are then capable of being optically transparent in addition to electrically conductive. It has also been shown that the grid pattern has an effect on the mesh performance, with hexagonal grid shapes having the highest transmittance-to-resistance ratio. [168] Similarly, silver NWs can be used in much the same fashion to create flexible, transparent, conductive films. [169] However, metal mesh and silver NWs, since they sometimes use silver, tend to still be more expensive than some organic options, such as conductive polymers. [166]

3.3.4.1.2. Conductive Polymers

Because of the limitations of inorganic transparent conductive materials, such as price and flexibility, many organic alternatives have been researched. As mentioned previously, a class of polymers exists that has electrically conductive properties. This class of polymers is also transparent and can therefore be used in TCF applications. Conductive polymers have lower conductivities than their inorganic counterparts, but they offer the benefit of mechanical

flexibility. Several articles discuss printing PEDOT:PSS as a TCF on flexible substrates to create devices such as organic solar cells, transistors, and displays. [170-172] Just like conductive polymers for conductive inks, these organic conductive polymers are typically used for lower performing flexible electronics applications due to their intrinsic lower conductivities, such as antistatic coatings and large area solar arrays. [20] Sheet resistance values below 1000 Ω/sq indicate current market leading performance in polymer-based transparent conductive materials.

3.3.4.1.3. Carbon-Based Materials

TCFs in general are fairly thin and fragile, and therefore have a tendency to show property degradation or material failure when exposed to mechanical stresses. [163] Carbon-based materials, such as CNT and graphene, can offer advantages over inorganic and conductive polymer materials regarding fragility. In addition to the properties of CNT and graphene discussed above, both CNT and graphene films are transparent. Therefore, there are several examples of these materials being used as TCFs for a variety of applications, including solar cells, OLEDs, and transistors. [173-175] Just like with any material, carbon-based TCFs have drawbacks. The resistance of these materials will need to be decreased before they are adopted into higher performing products, especially with the dual nature of CNTs (mixture of conducting and semiconducting forms). [169]

Linde Nanomaterials, located in San Marcos, California, has been working on creating CNT inks that can be used to create thin TCFs. [176] Linde Nanomaterials does not produce CNTs. They purchase CNTs from a commercially available source, and then purify those CNTs to produce CNT inks. The process that Linde Nanomaterials uses to purify CNTs and produce SWCNT inks is salt-enhanced electrostatic repulsion (SEER). This method involves reducing the SWCNTs in a metal/ammonia solution to make them negatively charged. They are then placed in a polar solvent, which enhances the electrostatic repulsion between the negatively charged tubes. This causes the individual nanotubes to begin to untangle and separate, ultimately leading to a solution of completely dispersed, untangled, individual charged SWCNTs. This process is extremely gentle, as it does not use sonication, functionalization, surfactants, or ultracentrifugation. Linde Nanomaterials intentionally purchases longer CNTs, and throughout the separation process, the length of the SWCNTs does not change. This is desirable because longer CNTs lead to decreased contact resistance. Linde's SEER Ink is used to create thin TCFs. [176] Because the separated, negatively charged SWCNTs are air sensitive, the ink must be applied in an inert environment to create these films. Minimum TCF requirements often quoted in literature are 90 percent transparency and 100 Ω/sq sheet resistance.

TCFs made with Linde Nanomaterials SEER Ink can exceed these values and reach approximately 92 percent transparency at 100 Ω/sq. While transparency and conductivity are important properties for TCFs, other properties, such as flexibility, hardness, adhesion, haze, environmental stability, and cost need to be taken into account as well, and Linde Nanomaterials is working to address these other properties as well. [176] Hardness and adhesion of SWCNT TCF can be thought of as being intrinsically linked, where increasing the adhesion also increases the hardness. Typically, SWCNT TCFs show very poor adhesion on glass. Linde Nanomaterials developed an undercoat that would lie between the substrate surface and the SWCNT layer. This coating does not functionalize the nanotubes, but they found that it can improve adhesion for very thin films. Additionally, applying the coating on top of the SWCNT layer as an overcoat

helps to increase the overall cohesion of the SWCNTs. Doping is often used to improve performance of the SWCNT TCF, but this often leads to a lack of environmental stability. However, the presence of the overcoat used to increase cohesion has been found to lock in the dopant and increase the overall stability of the film as well.

Linde Nanomaterials' SWCNT TCF were coated onto PET and polyethylene naphthalate (PEN) substrates and were compared to ITO coated on PET for flexibility performance. [176] Because of the brittle nature of ITO, the ITO coated PET did not withstand many flexing cycles. On the other hand, with the SWCNT-coated substrates, the substrates failed before the CNT coating did, demonstrating the extreme flexibility of the SWCNT inks. One of the problems with CNTs is that they are difficult, and therefore expensive, to produce at a suitable level of purity. [176] Linde Nanomaterials overcomes this hurdle by purchasing commercially available SWCNT and then simply processing them into their own SWCNT ink. This, in addition to their SEER process being fully scalable, enables them to produce SWCNT ink at a relatively low cost and at a relatively high performance level, in terms of resistance, transparency, adhesion, stability, flexibility, and cost.

In addition to CNT, numerous examples exist in literature of graphene being used as a transparent electrode to replace ITO, particularly in display and PV applications. In 2010, it was reported that 30-inch graphene films could be prepared by CVD on flexible copper substrates in order to create transparent electrodes. [177] In 2012, researchers from Korea published their work to create graphene anodes for flexible OLED applications. They modified the graphene anode to have a high work function and a low sheet resistance, and consequently were able to achieve luminous efficiencies that were significantly higher than devices with ITO anodes. [178] Similarly, in 2014, a group of researchers from Philips Research, the University of Cambridge, and Graphenea were able to achieve superior power efficiency with a graphene-based OLED as compared to a state-of-the-art ITO device. [179]

Additionally, researchers from Singapore and the United Kingdom published a paper in 2013 describing their use of graphene as a transparent conductor for organic solar cells. [180] They found that a higher transparency value could be obtained with four layers of graphene as compared to ITO. Even though graphene seems like an obvious choice for a transparent conductive material and there are many examples of graphene being used for that exact application, a few issues exist that would need to be addressed before graphene could be widely used. Probably the most common problem with graphene is getting it into a useable format. [181] Because it is so thin, it is difficult to remove it from the substrate on which it was grown and transfer it to a usable substrate, especially without causing defects and degrading performance.

As of December 2014, there was no cost effective and reliable way to perform this. GNP inks can be used instead of growing graphene in layers by CVD, but this results in lower performance with respect to both conductivity and performance and, besides cost, does not offer many other advantages over ITO or other ITO replacement technologies. [181] Another approach is to synthesize single crystal graphene onto semiconductor wafers, which Samsung has claimed to have performed, but this research is still in its infancy. Additional information regarding graphene for FHE applications can be found in Section 3.3.3 and Section 3.2. Specifically, a list

of companies involved in the graphene industry, particularly for FHE applications, is located in Table 5.

3.3.4.1.4. Comparison of ITO Replacement Technologies

Many reports and studies have been conducted to compare the various options for transparent conductive materials, with an emphasis on materials that can be used as replacements for ITO. Touch Display Research, Inc., founded by Dr. Jennifer Colegrove, is a technology market research and consulting firm that releases a semiannual report on ITO replacement technologies. [182] The report from May 2014 includes a graphic that displays how the different technologies stack up with regards to conductivity and cost. The information from the graphic is summarized in Figure 6.

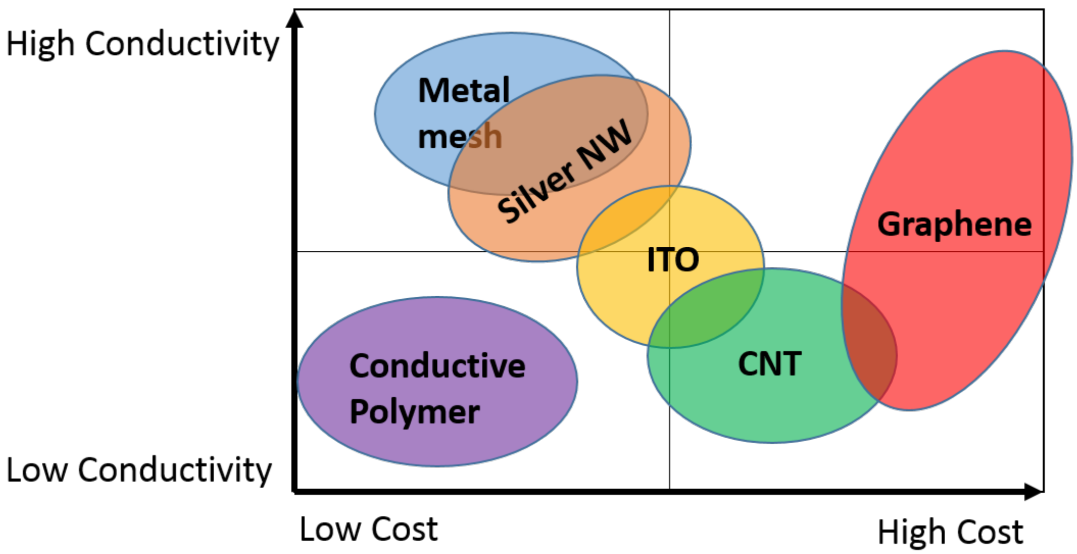


Figure 6. Conductivity versus Cost for Transparent Conductive Technologies [166]

Table 8 presents a list of several companies that offer transparent conductive coatings or films. Depending on the chemistry, these coatings range in performance, specifically regarding sheet resistance and percent transmission. Products that are metal-based offer the lowest sheet resistance values, while films that are carbon- or polymer-based are on the higher end of the resistance spectrum. However, graphene and CNT transparent conductive materials are the most highly researched for ITO replacement solutions, and the most expensive options as seen in Figure 6, most likely due to the new nature and recent and ongoing development of those technologies. [166]

Table 8. Specifications for Various Commercial Transparent Conductive Coatings

Company	Product Line	Conductive Material	Sheet Resistance (Ω/sq)	Transmission (%)
Cambrios (USA) [183]	ClearOhm™	Silver NWs	< 10 - 300	94 - 100
Carestream Advanced Materials (USA) [184]	FLEXX Transparent Conductive Films	Silver NW	~ 100	> 88
Canatu (Finland) [185]	CNB™ Films	Carbon	100 – 300	93.5 – 97.5
Cima NanoTech (USA) [186]	SANTE® TCFs	Nanoparticles	> 0 – 30	80 – 89
Heraeus (Germany) [104]	Clevios™	Polymer	< 200	~ 88
Nanogap (Spain) [187]	NGAP NF Ag-3101	Silver nanofibers	< 100	> 95
PolyIC (Germany) [188]	PolyTC® films	Metal mesh	5 – 30	> 85
Poly-Ink (France) [189]	Poly-Ink	CNT & polymer	150 – 1000	85 – 95
Rolith (USA) [190]	NanoWeb™	Metal mesh	1 – 20	93 – 97
XinNano Materials, Inc. (Taiwan) [191]	CNT-Based TCF	CNT	~ 400	> 89
Agfa-Gevaert (Belgium) [192]	Orgacon™ Aqueous S300 Coatings	Polymer	125 – 425	~ 90
Eikos (USA) [193]	Invisicon®	CNT	~ 250	> 90
BGT Materials (UK) [194]	Grat-Film™	Graphene	30 – 600	85 - 97
Graphene Laboratories (USA) [195]	Monolayer Graphene	Graphene	660 – 1500	>97
Graphenea (Spain) [196]	Monolayer Graphene on PET	Graphene	580	>97

In addition to the companies that are investing in ITO replacement materials, various universities and research organizations are doing the same. Industrial Technology Research Institute (ITRI) in Taiwan is focusing on PEDOT and metal mesh, which can be silver- or copper-based. [197] Other universities researching metal mesh and nanotubes include University of Illinois Urbana-Champaign, Stanford University, and Beijing Institute of Graphic Communication in China. In addition to ITRI in Taiwan, University of Cagliari and University of Bolgona in Italy; Kyung Hee University, Seoul National University of Science and Technology, and Korea Institute of Science and Technology in Korea; and University of Tokyo in Japan are interested in polymeric

replacements for ITO materials. As mentioned above, University of Exeter in the United Kingdom is researching a graphene material for transparent conductor applications that consists of two layers of graphene sandwiching molecules of ferric chloride. [132] Max Planck Institute for Polymer Research in Germany, University of Southern California, and University of Texas at Austin are all researching carbon-based ITO replacements. These universities and research institutes listed are just a sampling of the various entities working on ITO replacement materials, but it clearly demonstrates that research is being conducted all around the world for this technology.

3.3.4.2. Current Problems & Future Trends

The various problems associated with transparent conductive materials are essentially the same as the issues described previously for conductive inks. These problems include cost, performance, and processing. Since silver is an extremely popular and commonly used material for transparent conductive materials, efforts need to be taken to decrease the cost associated with this material. One way to address this issue is through the use of polymeric and carbon-based transparent conductors, and these materials offer superiority with respect to flexibility, but the electrical performance of these materials is still not up to par. Additionally, much more with transparent conductive materials than with conductive inks in general, transparency needs to be closely monitored and tailored to make sure that it falls within acceptable limits, and this becomes difficult as the thickness of the films increase. Processing is also sometimes an issue with transparent conductive materials as it is with conductive inks, including compatibility with roll-to-roll manufacturing and high temperature post-treatment methods.

Overall, with TCFs made from any of the materials mentioned, it is necessary to find a balance between the desired properties. A high electrical conductivity may require a tradeoff in transparency because as the thickness of the film increases, electrical conductivity increases while transparency decreases. [164] Additionally, as the thickness of the film increases, so does the cost of the film, especially when metal-based materials are being used. Therefore, as transparent conductive materials continue to be used for future flexible electronics applications, it is necessary to determine the most important properties for the desired application and try to choose materials that target those specific properties.

3.3.5. Conductive Epoxies

While conductive epoxies do not fall precisely within the functional ink family, they are important to briefly mention since they are often used with conductive inks. Conductive epoxies, which can be found in both traditional and flexible electronics, can be used in combination with or in place of conductive inks when adhesion to the substrate is extremely important or particularly challenging. Typically, the conductive epoxy adhesive is placed between a conductive ink trace on the substrate and a component that needs to be attached. [198] Unlike conductive inks that are traditionally solvent- or water-based, a conductive epoxy adhesive does not necessarily require liquid carrying agents. Instead, the epoxy can comprise a base agent (epoxy resin), a curing agent, and a conductive material to impart electrical conductivity. [199] Another difference between conductive epoxies and conductive inks is the mechanism by which they are hardened. Conductive inks harden through evaporation of the liquid carrier, while conductive epoxies cure through crosslinking of the epoxy resin initiated by the curing agent.

3.3.5.1. One-Part vs. Two-Part Composition

Conductive epoxy formulations can be one-part compositions in which all of the components are mixed together, and an additional energy source is required for curing to occur. [200] It can also be designed as a two-part composition, where the two parts of the formulation (binder and curing agent) are mixed together just before application to induce curing. Sometimes an additional activation source such as heat or UV can be used to enhance the cure of a two-part system.

There are advantages and disadvantages to one- and two-part compositions. One-part epoxies are easily managed due to the fact that there is simply one component. [201] Additionally, they typically have good heat resistance. Unfortunately, in order to cure the epoxy, an additional energy source needs to be used. Two-part compositions on the other hand do not require an additional energy source and begin curing as soon as the two parts are combined, most of the time at room temperature. However, the two different parts have to be properly measured and combined by the user, which requires more work and precision than a one-part epoxy.

3.3.5.2. Conductive Epoxies on the Market

DuPont (Table 12, item 38) offers a series of screen printable, thermoset, conductive single component epoxies that are cured with either anhydride or amine curing agents. [199] Creative Materials, Inc. (Table 12, item 12) just introduced their newest conductive ink which is a two-part epoxy ink targeted for adhesion to coated and low surface energy substrates characteristic of the printed electronics market. [202] Additionally, other companies including Conductive Compounds (Table 12, item 15) and Epoxy Technology (Table 12, item 13) offer conductive epoxy product lines targeted for printed electronics applications.

3.3.5.3. Current Problems & Future Trends

As substrates become more temperature sensitive, solder can no longer be used to for electrical connections. [203] Conductive epoxies can be utilized as a low temperature solder replacement, so it can be expected that the demand for conductive epoxy will increase as printed electronics become more popular. Conductive epoxies can be used in various avenues of the printed electronics industry, particularly in touch screens, solar cell circuits, and RFID applications. [202] Conductive epoxies will have problems in the future with the use of silver as the conductive material. [204] The high cost of silver makes it difficult to mass produce products at the consumer level. The tendency for silver migration (electromigration) is also a concern for high-performance materials. Electromigration is the gradual movement of metal atoms due to the momentum transfer caused by the flow of electrons. [205] Copper can be considered as a more economical alternative with a lower inclination to migrate, but research will have to be conducted to overcome its high susceptibility to oxidation. Additionally, bending of conductive epoxies tends to cause decreases in electrical conductivity, so this characteristic will need to be addressed as flexible substrates increase in popularity.

3.3.6. Dielectric / Insulating Inks

Dielectric materials resist the flow of electrons, functioning essentially as an electrical insulator. [206] In electronics applications, dielectrics can be used anywhere from components or devices (such as capacitors and transistors) to interlayers that prohibit capacitive coupling between interconnect lines. For printed electronics, dielectric inks carry out some of the exact same functions, but are applied through printing methods instead of conventional photolithography

techniques. Specifically, dielectric inks in FHE are used to enable multi-layer printing, ensure protection of various other layers, and prevent metal migration from conductive layers. [207] The aspects of a dielectric ink formulation, including a discussion of the benefits of organic versus inorganic dielectric materials, can be found below.

3.3.6.1. Ink Composition

A typical dielectric ink is a UV curable composition that includes an organic or inorganic dielectric material in a liquid carrier with binders and other additives. [208, 209] Examples of inorganic dielectric material include metal oxides, glass frit, ceramic particles, etc. [210] However, similar to conductive materials, organic dielectrics have become more popular in recent literature due to their ease of printing, availability, and adequate performance. [211] Two organic dielectric materials heavily used are polyimide (PI) and poly-4-vinylphenol (PVP). PI is a low cost option, but PVP exhibits better performance. Whether an organic or inorganic dielectric material is utilized, they are dispersed/dissolved in an organic solvent, such as hexanol or ester alcohol. Just like with conductive inks, a binder is used in order to hold the formulation together and improve adhesion to the substrate. In a patent, U.S. 6,356,234 B1, from June 1997, a binder appropriate for a dielectric ink composition is described as a hydrocarbon resin containing a styrenated alkyd. [209]

In addition to the solvent, dielectric, and binder, additives such as a drying agent or a tack reducing agent can be included. These types of additives will be explained in more detail in Additives for Functional Ink Formulations, Section 3.3.10. Dielectric inks need to be homogenous and thin, with low surface roughness since they often serve as substrates for subsequent ink layers. [208] Because a smooth surface is so important for dielectric layers, defoaming additives are often used in order to eliminate the bubbles and foam that can be formed from high speed processing of the ink. [212] Additionally, holes are typically needed in the dielectric layer so that connections can be made through the layers. [208] These holes are generated in the printing of the dielectric, and if the viscosity is too low and the wetting of the ink is too high, these holes would be difficult to create. Because of these requirements, depositing dielectric material through atomic layer deposition (ALD) is often preferred in order to produce an optimal dielectric layer. [213]

3.3.6.2. Inorganic vs. Organic Materials

Silicon dioxide has been one of the most commonly used dielectric materials for a variety of reasons, including the fact that its large band gap and low bulk trap and defect density typically lead to a low leakage current. [214] Additionally, since silicon dioxide can be formed by oxidizing an already existing layer of silicon, the dielectric layer could be formed in a very uniform manner and can result in a high quality interface. [215] Unfortunately, silicon dioxide has a relatively low dielectric constant which leads to a lower capacitance by design, but decreasing the thickness can help increase the capacitance. [214] However, as electronics, and therefore the layers of dielectric materials, are becoming thinner, the tendency for dielectric layers, including silicon dioxide, to demonstrate leakage is increasing, and the increasing leakage current is overpowering the increasing capacitance in silicon dioxide layers. One way to address this problem is to use inorganic materials with higher dielectric constants, because that could allow the necessary charge to accumulate at lower voltages. [212] Unfortunately, these inorganic materials present their own set of issues.

Inorganic metal oxides, which are traditionally vacuum deposited, can be prepared for printed application methods but typically require additional surface modification. [214] Inorganic dielectric layers can have poor compatibility with organic semiconductors, and their rigid mechanical properties often rule them out for flexible electronic devices. For these reasons, polymeric dielectric materials have been sought out as an alternative to conventional inorganic dielectrics. [214] The polymer-based formulations allow for much more mechanical flexibility, but at the cost of reduced dielectric constants (and therefore reduced capacitance) and the need for larger gate thicknesses to avoid leakage currents. Crosslinking polymers have been studied as an attempt to harness the increased flexibility while decreasing the amount of gate leakage. Crosslinking also helps to increase the durability of the organic dielectric layer so that subsequent layers can be placed on top of the dielectric layer.

To take advantage of the benefits that both inorganics and organics offer, hybrid dielectric systems have been researched more recently. [214] These systems can involve inorganic nanoparticles dispersed in a polymer matrix. This option could be limited by the ability to disperse the particles, but additives such as agglomeration protectors and others discussed in Section 3.3.10 can help address this issue. Inorganic and organic layers can also be stacked on top of one another to form a hybrid dielectric system. This could potentially address compatibility issues that would result from inorganic dielectric materials being laid on an organic substrate. Much of the recent academic work in printable dielectric compositions has revolved around these hybrid systems.

In 2005, a team comprised of researchers from Bell Laboratories, DuPont Central Research, and Air Force Research Laboratory (AFRL) published an article describing their work on dielectric materials for flexible electronics applications. [216] They discuss organic/inorganic core shell nanoparticles that were synthesized using high K TiO_2 as the core nanoparticle and polystyrene as the shell. This material, which has been incorporated into capacitors and TFTs, is easy to process into transparent continuous thin films, and demonstrates a dielectric constant enhancement of over three times that of bulk polystyrene. Another article was published in 2008 describing work performed at Yonsei University in Korea. [217] Researchers created a functional dielectric ink suitable for inkjet printing using a thermally crosslinkable organosiloxane-based organic-inorganic hybrid material. Through their studies, they discovered that the ink solvent chemistry plays an extremely important role in the formation of uniform dielectric layers, and they found that using a combination of high boiling point and low boiling point solvents worked best to create organic thin-film transistors (OTFTs).

In 2012, researchers from Northwestern University described their work to integrate hybrid inorganic-organic gate dielectric materials with CNT materials in order to create a CNT transistor device. [218] They claim that by combining high-purity semiconducting CNT films with custom-designed hybrid inorganic-organic gate dielectrics, a synergistic effect leads to improvements in transconductance, intrinsic field-effect mobility, sub-threshold swing, and on/off ratio. Their formulations are compatible with low temperature, large-area processing and are applicable for low-power TFT-based electronics.

3.3.6.3. Material Property Comparison

Table 9 provides data for the dielectric constant, resistivity, and breakdown voltage of various inorganic and organic dielectric materials. The dielectric constant, also called relative permittivity, is the factor by which the electric field between two point charges in a material is increased or decreased relative to vacuum. [219] The dielectric constant is designed to be either high or low, depending on the application. [212] High dielectric constant materials can be used to decrease the operating voltage. Low dielectric materials may be desired to reduce parasitic capacitance and trapping density at the dielectric/semiconductor interface.

According to the Large Area Flexible Electronics chapter in the International Electronics Manufacturing Initiative (iNEMI) 2013 Technology Roadmap, commercially available dielectric materials have permittivity values ranging from 2 to 20, but a few researchers have actually been able to achieve higher values. [220] Electrical resistivity is an intrinsic property of a material that describes how strongly the material resists the flow of electric current. [134] Because a dielectric material is designed to resist the flow of electricity and provide insulation, it is desirable for the resistivity to be as high as possible. Dielectric strength or breakdown voltage is defined as the maximum electric field that a material can withstand without breaking down and experiencing failure of its insulating properties. [221] Dielectric strength is typically measured as a voltage per unit length, and a high value is desirable in order to avoid the need for frequent replacement of a dielectric material within a device or system.

Table 9. Properties of Various Dielectric Materials

Material	Dielectric constant / relative permittivity	Resistivity (Ω·m)	Breakdown voltage/ dielectric strength (MV/m)
Glass	4 – 7 [222]	1011 – 1015 [134]	9.8 – 13.8 [221]
Porcelain (ceramic)	6 – 8 [222]	1 x 1012 [223]	4 [224]
Mica	5 [225]	1 x 1013 [226]	118 [221]
Dry air	1 [222]	1.30 x 1016 – 3.30 x 1016 [134]	3.0 [221]
Distilled water	80 [227]	1 x 1010 [223]	65 – 70 [221]
Vacuum	1 [222]	Infinite (in theory)	1012 [221]
Helium (gas)	1 [228]	N/A	0.15 (relative to nitrogen) [221]
Nitrogen (gas)	1 [229]	N/A	1.0 (by design) [221]
Paper	3.8 [219]	108 [230]	14 [224]
Fused silica	3 [225]	7.5 x 1017 [134]	25 – 40 [221]
Silicon	11.8 [222]	6.40 x 102 [134]	30 [231]
Silicon dioxide	4.5 [222]	1 x 1013 [232]	560 [233]
Magnesium oxide	9 [225]	1012 – 1013 [234]	6 - 10 [235]
Aluminum oxide	9 [225]	1 x 1014 [232]	17 [236]
Polypropylene	2.2 [222]	1013 [237]	23.6 [238]
Polyethylene	2.3 [222]	1013 [239]	18.9 [238]
Polyimide	3.4 [219]	1016 [240]	22 [240]
Poly-4-vinylphenol	4.0 – 5.2 [241]	Unknown	Unknown

3.3.3.5. Dielectric Inks on the Market

In addition to the large amount of research that is being conducted in academia regarding inorganic, organic, and hybrid dielectric materials for FHE applications, a considerable number of companies are also involved in the dielectric ink market. DuPont (Table 12, item 38) has a line of solventless UV-curable dielectric inks for screen printing applications on both rigid and flexible electronics for membrane touch switch materials and touch sensor materials. [242] Engineered Materials Systems, Inc. (Table 12, item 58) offers two different VOC-free acrylic dielectric inks that are UV-curable. [243] Henkel (Table 12, item 49), in addition to many other printed electronics inks, offers five UV-curable dielectric inks for various markets, including consumer, displays, medical, and RFID. [244] Merck has polymers for dielectrics that are customizable and integration friendly. [245] These polymers are compatible with a variety of large scale printing methods, have the potential to pattern down to less than 5x5µm features, allow for surface energy and hardness control, and have excellent electrical performance. Commercial dielectric inks can sometimes be heat cured instead of UV cured. One example is CCD-120A, a thermally conductive dielectric ink produced by Caledon Controls Ltd. (Table 12, item 70). [246]

3.3.6.5. Future Trends

The future of dielectric inks will be in continuing research to determine which one of these technologies (inorganic, organic, or hybrid) provide the best set of trade-offs for FHE, particularly regarding efficiency, cost, and manufacturing. [211] Organic dielectrics have an unknown stability and generally lower dielectric constants than what inorganic dielectrics can provide. Inorganic dielectrics have not shown promise as a low cost option, or as ones than can be easily incorporated with organic materials. Hybrid dielectric systems might just be the best option for printed electronics, combining the advantages of both material classes while attempting to minimize their disadvantages.

3.3.7. Semiconductor Inks

A semiconductor is a material that exhibits electrical conductivity between that of a conductor and an insulator. This means that its electrons are not free flowing to conduct electricity like a conductor, but they have a better chance to become free flowing than an insulator's electrons. In order to conduct electricity, these electrons need gain energy to move to higher states, or bands. [20] In an inorganic semiconductor, the region that is filled with electrons and does not contribute to conduction is known as the valence band. Above the valence band is the band gap, which is the energy barrier than an electron needs to cross to get into the conduction band, where electrons can freely move about and contribute to electrical conductivity. A semiconductor can be doped to enhance its conductivity by either adding or removing electrons. (P-type semiconductors have missing electrons, or holes, in their structure, while n-type semiconductors have extra electrons. [247]) Semiconductor materials are the backbone of electronic devices, with silicon being the most popular and widely used semiconductor material throughout the industry. [248] Therefore, being able to incorporate semiconducting materials into ink formulations for printed electronics is extremely important. The following paragraphs will describe the various components that make up a semiconducting ink formulation for FHE applications.

3.3.7.1. Ink Composition

Semiconductor inks can be based on organic or inorganic semiconducting materials. Inorganic semiconductor inks involve fabricating silicon, or any other inorganic semiconductor, into a particle through solution processing. [249] This semiconducting particle can then be combined with various other components to create an ink. On the other hand, organic semiconductors, which can be small molecule or polymeric and even carbon-based, can be fabricated into semiconducting inks as well. Most inorganic semiconductor inks are based on silicon nanoparticles. In August 2009, NanoGram Corporation (Table 12, item 60) announced the successful fabrication of the first TFT produced with an inorganic semiconducting ink. [249] This printable ink, based on nano-scale crystalline silicon particles, can be applied through inkjet or spin coating. NanoGram Corporation's patent application for similar technology, U.S. 20130221286, filed in April 2013, describes the semiconducting ink formulation. In this patent, the ink formulation is simply the silicon nanoparticles dissolved in an organic solvent, such as ethylene glycol or terpinol, but this formulation can be tailored depending on the various printing applications and processing methods. [250] This patent also describes germanium as a semiconducting material with similar properties to silicon and says that it can be used as an alternative to or as an alloy with silicon, substituting germanium or silicon germanium nanoparticles for silicon nanoparticles.

Typical organic semiconductor ink formulations, like the ones found in Fuji Xerox patent application U.S. 8,716,703 B2 from May 2012, simply include the organic semiconductor material in an organic solvent like toluene. [251] Other formulations can include a metal containing compound to serve as a catalyst or a crosslinking agent for the polymer if necessary, as demonstrated in Samsung's patent application U.S. 8,816,330 from 2011. [252] While not much explicit information can be found on the subject, semiconductor inks for printed electronics seem for the most part to be thermally cured. One report from the Journal of Materials Chemistry mentions a thermal cure mechanism for semiconductor nanoparticle inks, specifically metal oxide nanoparticles. [253] Additionally, in the Fuji Xerox patent application listed above, a method is described where the semiconductive polymer in solvent is heated in a nitrogen atmosphere to cure and form the organic semiconductor layer. [251]

3.3.7.2. Inorganic vs. Organic Materials

As mentioned above, semiconducting ink formulations can be either organic or inorganic. Organic semiconductor materials are organic materials that demonstrate electrical conductivity between that of insulators and metals. [254] One category of organic semiconductors is small molecules, which typically includes hydrocarbons like pentacene, anthracene, and rubrene.

Organic semiconductors can also be polymeric, such as polythiophene, polyphenylenevinylene, and polyfluorene. Some companies, such as Merck, produce both small molecule and polymeric organic semiconductor material. [245] There are many advantages of organic semiconductors over inorganic, such as ease of fabrication, mechanical flexibility, fabrication temperature, and occasionally cost [255], but they sometimes still fall short in terms of stability, performance, and even cost depending on how new the material is. [212]

Polymeric semiconductors, often called synthetic metals, are beneficial because they can be solution-processed and printed, but they often have air sensitivity, insufficient mobility,

purification issues, and short lifetimes. [256] Small molecule organic semiconductors have higher mobilities and performance than polymer electronics [20], but the mobilities of both organic small molecule and polymeric semiconductors are only at best comparable to amorphous silicon. [257] The mobilities of charge carriers in organic semiconductors have values typically around 10-2 cm2/Vs, where inorganic semiconductors are on the range of 100 – 1000 cm2/Vs. [258] This lower performance is due to the narrow bandwidth arising from the weak interactions between the molecules in organic semiconductors.

Materials have been developed to help increase the mobility of organic semiconductors, but the processing and printing of these materials often leads to decreased mobilities compared to the bulk. [256] Small molecule organics can be deposited more easily, such as through epitaxy methods, compared to polymeric semiconducting materials that need to be high-vacuum processed to achieve performance values close to inorganic materials. [20] Organic single crystals can have mobilities almost a factor larger than polymer semiconductors, but this increased mobility of the high-purity single crystals is still lower than that of polycrystalline silicon. [256] [257] These materials are also subject to air sensitivity and complex processing conditions which makes them not as suitable for high-speed printing techniques. In polymer semiconductors (and conductors), the electrons move freely in the lowest unoccupied molecular orbital (LUMO), which is just above the band gap and is synonymous with the conduction band in inorganic materials. [20]

When electrons are in the LUMO or conduction band, the material is more reactive and therefore more prone to oxidation. Semiconductors that function through electron transport (n-type) have many more electrons in this band and are therefore much more unstable and subject to oxidation. This causes p-type organic semiconductors to be much more prevalent than n-type. [255] Unfortunately, organic semiconductors can only be useful if both types are incorporated, and ideally, electron and hole transport should be balanced. [20] In January 2009, Polyera Corporation (Table 12, item 53) from Illinois demonstrated that a polymer based on naphthalene-bis(dicarboximide) could be used as an n-channel material. [259] Since then, more companies have been able to research further into both n-type and p-type organic semiconducting materials.

Sigma-Aldrich (Table 12 item 42) offers various small molecule and polymeric organic semiconductors that function as both n-type and p-type materials and are targeted specifically for inks for printed electronics. [260] In an inorganic semiconductor, the electrons and holes from doping create new bands within the band gap, decreasing the energy an electron would need to reach the conduction band. [20] Polymer semiconductors are doped through other mechanisms. During redox reaction doping, which usually occurs to create a p-type semiconductor, the dopant reacts and becomes an anion by removing electrons and leaving holes in the polymer backbone. Organic semiconductors can also be doped through acid-base reactions, which is what happens with PEDOT and PSS. The negatively charged PSS counterbalances the positively charged PEDOT. The doping level in a polymer semiconductor is defined as the ratio of the number of counter-ions to the number of monomers in the chain. High levels, such as greater than or equal to 15%, are undesired because of the possibility of changing the chemical nature of the chain, but these high levels are sometimes necessary to achieve acceptable conductivity.

Inorganic semiconductors for printed electronics solve the low mobility and stability issues, but high temperatures are required in order to produce high-quality films of these materials. [257] Therefore, inorganic semiconductors are difficult to use with the temperature sensitive substrates common for printed electronics like plastic and paper. Inorganic semiconductors have much higher charge carrier mobilities, which makes them more suitable when high switching speeds are necessary [212], whereas organic semiconductors have found application in other areas, including solar cells and OTFT, OLEDs, organic field effect transistors (OFET). [260] Inorganic semiconductor materials also have complex processing systems, but steps are being taken to attempt to address these issues. [257]

3.3.7.3. Recent Developments

Some carbon-based materials discussed previously that are used as conductors can also be used as semiconductors. Depending on their atomic arrangement, CNTs can display both metallic and semiconducting characteristics. [261] Typically, today's CNTs are produced as a mixture of conducting and semi-conducting forms. [111] SWeNT (Table 12, item 29) takes advantage of this fact and with their proprietary catalyst offers a line of CNT inks that have up to 95 percent semiconducting content. [115] CNT semiconducting films can offer extremely high performance, optical transparency, and increased stability compared to other organic semiconducting materials. [257] Even though some companies like SWeNT take advantage of the dual nature of CNTs (mixture of conducting and semiconducting forms), it can pose problems if it is necessary to remove either the conducting or semiconducting form from the composition before use, as this can be a time consuming and difficult production step. [212] Therefore, devices using CNT inks sometimes have a tradeoff between mobility and on/off ratio. It is believe that smaller diameter CNTs could lead to better on/off control but perhaps lower mobility. [262]

Various methods for separating and purifying CNTs have been investigated in the recent years, and Chasm, with its partner SWeNT, is one of the companies investing in this area. Chasm is a small consulting group with laboratory capabilities located in Massachusetts. They are linked with SWeNT in that the Vice-President of Applications Development of SWeNT, Robert Praino, is also a Co-Founder of Chasm. Additionally, Chasm performs all of the applications development for the materials developed by SWeNT. In typical CNT manufacturing processes, the CNT product out of the reactor is 33% metallic and 67% semiconducting. SWeNT is looking to purify these materials using chiral separation. The hypothesis is that chiral separation and increased purity will lead to improved performance.

SWeNT and Chasm are using an aqueous two phase extraction method to separate metallic and semiconducting SWCNTs, and they are currently working on a scale-up effort for this chiral separation process. [262] [263] They have modified their separation process and claim that they can achieve approximately 99% semiconducting content. They formulated several different types of inks using their purified semiconducting CNTs, and, with regards to aggregation, discovered that semiconducting SWCNTs in organic solvent are much less stable than semiconducting multi-walled carbon nanotubes (MWCNTs) in organic solvent. Semiconducting SWCNTs are more stable in aqueous solvents than organic solvents, but there are still not as stable as MWCNTs.

Chasm is beginning to print TFTs with their semiconducting CNT ink, and they are trying to determine if the higher purity materials actually lead to better device performance. Their design process for building a TFT includes formulating an ink for a stable inkjet process, printing silver source and drain, printing semiconducting CNT layer, coating dielectric, and coating silver gate. They are continuing the separation process development and scale-up. Additionally, they are beginning to look at the enriched metallic phase instead of focusing only on the semiconducting phase. Additionally, some of the most recent developments in the semiconductor ink industry have involved zinc oxide materials. "The high electron mobility, high thermal conductivity, wide and direct band gap and large exciton binding energy make zinc oxide suitable for a wide range of devices, including transparent TFTs, photodetectors, light-emitting diodes and laser diodes that operate in the blue and UV region of the spectrum." [264] However, despite the recent developments, controlling the electrical conductivity of zinc oxide has remained a challenge.

Some groups have reported the creation of p-type zinc oxide, but reproducibility and stability are an issue. Zinc oxide nanorods have been studied with the goal to produce p-type semiconductors for printed transistors and OLEDs. [265] Within this research, the crystal growth mechanisms for zinc oxide are being studied so that the composition, diameter, growth position, and orientation of the NWs can be controlled, hopefully leading to precisely engineered electronic devices. In 2010, researchers from National Tsing Hua University in Taiwan reported that they were able to grown aligned zinc oxide nanorods directly onto paper substrates. [266] Using these zinc oxide nanorod arrays, they created prototype photoconducting devices and PN junction diodes. A few researchers are combining zinc oxide materials with polymers to create electronics for PV applications. In 2004, researchers from Eindhoven University of Technology in The Netherlands released a paper describing a semiconductor material consisting of n-type nanocrystalline zinc oxide nanoparticles and conjugated polymers in organic solvent. [267] These materials were spin-cast into thin films on a transparent glass substrate coated with ITO and PEDOT:PSS to create efficient hybrid PV cells with a high fill factor and open-circuit voltage.

Similarly, a team from National Renewable Energy Laboratory (NREL) and Colorado School of Mines published a paper a year later describing their work to create hybrid PV devices using polymer and zinc oxide nanofiber composites. [268] Their composites take advantage of both the high electronic mobilities of oxide semiconductors and the low-temperature solution-processability of polymeric materials. As mentioned above, zinc oxide materials are also being investigated as semiconductors for transistors. In 2005, researchers from the University of Cambridge in the United Kingdom published a paper detailing their work in this area. [269] They describe that by controlling the shape of the zinc oxide nanocrystals (from spheres to rods), the semiconducting properties of the spin-coated zinc oxide films could be improved. They observed that increasing particle size and aligning the nanorods along the substrate appear to help improve performance of the thin-film field-effect transistors that were created with this technology. A few years later, a team comprised of researchers from Purdue University, Northwestern University, and University of Southern California described their fabrication of fully transparent NW transistors. [270] They created both indium oxide and zinc oxide NW transistors, which exhibited high carrier mobilities compared with bulk or TFTs made from the same materials.

They anticipate that their NW transistors will be applicable in active matrix organic light emitting diode (AMOLED) displays.

3.3.7.4. Material Property Comparison

Table 10 provides data for the band gap, electron mobility, and hole mobility of various organic and inorganic semiconductor materials. The band gap of a material is the minimum amount of energy required to excite an electron from the valence band to the conduction band. [271] The desired value for the band gap of a semiconductor is dependent on the particular application. The most highly used semiconductor, silicon, has a band gap of approximately 1 eV, but wide band gap semiconducting materials exist that have band gaps of at least 3 eV. [272] This higher band gap would allow devices to operate at much higher voltages, leading to more powerful electronics. On the other hand, if a lower voltage device is desired, a material with a smaller band gap would be more appropriate. By conventional standards, any polymer with a band gap below 1.8 eV is considered a low band gap polymer. [20] Electron mobility and hole mobility are very similar concepts. Electron mobility is a value used to characterize how quickly an electron can move through a material when pulled by an electric field. [273] Hole mobility represents a similar value but regarding holes instead of electrons. Ideally, electron and hole mobility values would be high for optimal semiconductor performance.

Table 10. Property Data for Common Semiconductor Materials

Material	Band Gap (eV)	Electron mobility (cm2 V-1s-1)	Hole mobility (cm2 V-1s-1)
Inorganic			
Silicon	1.12 [274]	≤ 1400 [275]	≤ 450 [275]
Germanium	0.67 [274]	≤ 3900 [275]	≤ 1900 [275]
Gallium arsenide	1.42 [274]	≤ 8500 [275]	≤ 400 [275]
Indium phosphide	1.351 [274]	≤ 5400 [275]	≤ 200 [275]
Indium antimonide	0.17 [274]	≤ 7.7 x 104 [275]	≤ 850 [275]
Indium arsenide	0.356 [274]	≤ 4 x 104 [275]	≤ 5 x 102 [275]
Gallium phosphide	2.22 [274]	≤ 250 [275]	≤ 150 [275]
Gallium antimonide	0.725 [274]	≤ 3000 [275]	≤ 1000 [275]
Silicon carbide	2.86 [274]	≤ 900 [275]	≤ 320 [275]
Gallium nitride	2.34 [274]	≤ 1000 [275]	≤ 350 [275]
Zinc oxide	3.37 [276]	≤ 200 [277]	≤ 50 [277]
Organic			
Pentacene	1.82 [278]	N/A	≤ 5.5 [279]
Anthracene	2.1 – 3.9; 3.72 [280] [281]	≤ 9 [282]	~1 [283]
Rubrene	2.2 [284]	≤ 0.81 [285]	≤ 40 [279]
Polythiophene	~2 [286]	N/A	≤ 0.02 [287]
Polyphenylenevinylene	2.4 [288]	N/A	≤ 0.43 [287]
Polyfluorene	~1.3 (as a copolymer) [289]	N/A	≤ 1.1 [290]
Naphthalene bis(dicarboximide)	Unknown	≤ 0.7 [291]	N/A
Graphene	N/A	2 x 105 [292]	≤ 4500 [293]
CNT	0 – 2 [112]	7.9 x 104 [292]	≤ 10,000 [294]

3.3.7.5 Future Trends

As demonstrated, inorganic and organic semiconductor systems for printed electronics have both positive and negative attributes. The small molecule and polymer organic semiconductors perhaps have the upper hand solely because they are more fully explored for printed electronics applications as compared to inorganic particle formulations. [257] However, despite this fact, the advantages and disadvantages of both systems make it difficult to determine just what direction the industry will go, but with so many options, it is likely that semiconductor materials for large area printed electronics will become a more tangible reality in the future. More applications for printed semiconductors could be reached with the development of semiconducting ink materials with increased carrier mobilities, increased stability, and less demanding processing conditions. [212, 257]

3.3.8. Resistive Inks

In some cases, high conductivity is not necessary, and higher levels of resistance can be tolerated or even desired, depending on the particular application. Similar to how resistors impart electrical resistance in a circuit, resistive inks can reduce the current flow in a printed electronics device. Sometimes, through these resistive mechanisms, the composition can generate heat, which is the premise behind printed resistive self-limiting heater technology. [295] Additionally, resistive inks can provide lubricity, protection for conductive surfaces, and prevention of silver migration, much like the dielectric inks. [244]

3.3.8.1. Ink Composition

Resistive ink formulations are very similar to conductive inks, but the metal or other conductive element is replaced with a resistive element, which is most commonly carbon. [54] The carbon used in these compositions usually comes in two forms: graphite (grey-black platelet form) and carbon black (jet-black amorphous form). The benefit of using carbon over silver, besides the cost advantage, is the freedom that it provides to formulate inks of varying resistivity. Carbon can also be blended with silver to create an even wider range of possible resistivity values. In addition to some form of carbon, typical resistive ink formulations include an organic solvent, binder, and additives, such as antioxidants or dispersing agents. [209] Resistive ink formulations are subject to a heat curing step after printing to remove the solvent. [54]

3.3.8.2. Resistive Inks on the Market

Methode Electronics, Inc. (Table 12, item 21) has a line of resistive carbon inkjet inks that contain carbon nanoparticles and are suitable for use in sensors, secure packaging, lighting, RF shielding, and toys. [67] DuPont (Table 12, item 38) has a carbon conductor called DuPont 7082 that can also be used as a polymer thick film resistor. [296] Henkel (Table 12, item 49) has a portfolio of resistive carbon inks for printed electronics, mainly solvent-based, for a variety of end applications, including consumer, medical, and automotive. [244] Henkel’s inks can also be used with several different substrates, including PET films, paper, membrane touch switches, and rigid PCBs.

3.3.8.3. Current Problems & Future Trends

Because resistive inks are a simple and fairly well-established technology, as demonstrated by the companies described above that are producing these inks, very few examples of universities and research institutes investing in resistive inks development could be found. However, even

though resistive inks are well-established, there are still some aspects that could be addressed for better use for flexible electronics in the future. Both graphite and carbon black tend to have wide variation in their respective properties, which leads to batch-to-batch inconsistencies for resistive inks made with these materials, including inconsistent rheological and electrical properties. [297] Therefore, one issue that needs to be address is eliminating the variability in properties of both carbon black and graphite. Additionally, the temperature coefficient of resistance (TCR) of carbon and graphite is relatively large in magnitude, and therefore a resistor resulting from the use of inks containing these materials will not exhibit high stability when subjected to temperature changes. This property can be effectively utilized in some applications, but it could be undesirable in others and would need to be addressed to be useful for those other applications.

3.3.9. Other More Specialized Inks

In addition to the main types of inks used for flexible electronics, which includes conducting, semiconducting, dielectric, and sometimes resistive, other less common inks, such as EL inks and magnetic inks, can be used for specialized applications. A brief description of these inks and the various applications they are used for can be found in the following paragraphs.

3.3.9.1. Electroluminescent Inks

EL materials, such as phosphors, are materials that emit light in response to an electric current or strong electric field. [298] These types of materials can be formulated into FHE inks for specific application in EL lamps and light emitting devices and displays. [299] Typically, these inks consist of a phosphor material in a polymeric matrix and/or solvent. There are several examples of these types of formulations in industry. A patent application for an EL ink was filed in September of 2009 by Add-Vision, Inc. [300] Their invention was an organic solvent composition that included an EL polymeric material and a combination of salts to promote ionic mobility, thermal and electrochemical stability, compatibility, and solubility.

DuPont (Table 12, item 38) has a line of EL materials called LuxPrint, whose formulations consist of several different phosphors within polymer matrices. [299] LuxPrint materials are designed for heat curing and can be used in screen printing applications. In addition to Add-Vision Inc. and DuPont, Caledon Controls Ltd (Table 12, item 70) offers thermally-cured phosphors in a variety of colors that produce varying brightness levels. [301] These materials are one-component phosphors pastes designed for EL lamp fabrication. While EL inks allow flexible electronics to dive into light emitting applications, there are unfortunately some disadvantages.

Typically, EL inks have a lower power efficiency than other traditional lighting materials. [302] Additionally, the shelf life of these products are sometimes unpredictable. Therefore, in order for printed EL displays and EL inks to become more mainstream, they need to achieve the same performance levels as traditionally manufactured graphics displays.

3.3.9.2. Magnetic Inks

Magnetoelectronics is a very important segment of modern electronics, but very little work has been performed to demonstrate the feasibility of printable magnetoelectronics. Materials with sufficient permeability and permittivity values have wide application areas in the electronics industry today, including for magnetic sensors and antennas, and there is a need for printable materials with magnetic functionalities, especially for advanced high frequency applications.

[303] A few examples of research being conducted in this area have emerged in the past couple years, and these are detailed below.

A paper was released in 2010 titled "Formulation of Screen Printable Cobalt Nanoparticle Ink for High Frequency Applications" that described work performed by the EMPART Research Group at the University of Oulu in Finland. [303] They investigated the feasibility of using magnetic nanoparticle-containing inks to create materials with high permeability that can be used as an ink for printed electronics, specifically in antenna substrates and magnetic sensors. Their screen printable formulation included cobalt nanoparticles that were surrounded by a surfactant, rheology modifier, binder, and organic solvent. During the various experiments, the ratios of the components were optimized, but all of the formulations were subjected to a heat cure in order to evaporate the volatile components. Their work proved that these magnetic nanoparticle ink compositions demonstrated a relatively high permeability and could be used in printed electronics. The main problem with these formulations, and with nanoparticle inks in general, is the stabilization of the particles in suspension. Choosing the right surfactants and stabilizers can certainly help this problem, but some of the formulations still demonstrated agglomeration, especially at higher particle loadings. While these formulations were effective for what they were trying to accomplish, future work with these inks will most likely involve stabilization of the magnetic particles in the compositions. An article was released in July 2012 describing a printable magnetic sensor. [304] Up until this point, the lack of appropriate sensing compounds that work at ambient conditions made the fabrication of printable magnetoelectronics challenging.

A team at IFW Dresden in Germany addressed this issue and successfully fabricated the first printable magnetic sensor that relies on the giant magnetoresistance (GMR) effect. (The GMR effect is the change in electrical resistance of some materials in response to an applied magnetic field. [305]) As part of this work, they developed magneto-sensitive ink that can be painted on any substrate, and they mention that instead of painting, other roll-to-roll methods could be employed, such as flexography, spray coating, and screen printing. The team integrated the printed GMR senor into a hybrid electronic LED circuit. With this new invention, they triggered the LED on/off state with a permanent magnet that modifies the resistance of the printable magnetic sensor and alters the current flow through the LED. While these results are exciting, many issues still need to be sorted out, such as high-volume production of the magneto-sensitive ink and demonstration of large-scale printing of the ink.

In April 2015, VTT Technical Research Centre of Finland developed a new, cost-efficient method of producing various types of metallic nanoparticles that can be used in applications for conductive and magnetic inks. [306] Their aerosol technology reactor can efficiently and cost-effectively produce kilograms of nanoparticles per day. The nanoparticle synthesis is performed at ambient air pressures and relatively low temperatures. As part of their work, VTT used the nanoparticles they synthesized to manufacture magnetic inks for magnetic field sensors. VTT is working to further scale and commercialize their nanoparticle reactor technology. Overall, magnetic inks are still very much in the R&D stage, and no commercial example of magnetic inks for printed electronics could be found to date. Significant achievements have been achieved, but as research progresses for magnetic inks, solutions will have to be found for magnetic nanoparticle aggregation, high-volume production, and large-scale printing issues.

3.3.10. Additives for Functional Ink Formulations

It is common for chemical products to contain additives that, while not directly responsible for the main function of the product, enhance product characteristics or prevent premature product deterioration. In the case of inks used in printed electronics, common additives include binders, aggregation preventers, and oxidation protectors, among others. These three additives will be described in detail below. Table 11 summarizes other additives commonly used in ink formulations and explains the function they carry out within the composition.

3.3.10.1. Binder

To help the ink adhere to the substrate, ink formulations include a binder, typically a resin. [64] When the solvents evaporate, the binder is left behind to promote adhesion and particle packing. [54] Increasing the amount of binder content helps to ensure adhesion to the surface, but it also could lead to a decrease in conductivity or other functionality. The binder can disrupt electron flow and prevent conductive particles from touching and forming continuous conductivity. [64] Therefore binder content needs to be monitored in order to obtain a delicate balance between adhesion and conductivity.

3.3.10.2. Aggregation Protection

The components in ink formulations have a tendency to clump together, so they often need to be protected from aggregation in order to have the most efficient performance. Since the high surface area of nanoparticles can lead to increased agglomeration, formulations involving nanoparticles in particular must have aggregation protection. [212] Protection against aggregation can be achieved through either an electrostatic or a steric mechanism. [64] Electrostatic stabilization is caused by electrostatic repulsion between electrical layers surrounding interacting particles, with higher electrical potential of a particle causing more repulsion and therefore more stability. However, this electrostatic mechanism is not effective in all solvents of interest. Therefore, steric stabilization is sometimes preferred as its effectiveness is not as dependent on the components in the system. Steric stabilization refers to surrounding the particles with a layer of sterically bulky molecules in order to keep the particles away from each other. In some cases combining these mechanisms leading to electrosteric stabilization is a highly effective way to reduce aggregation.

3.3.10.3. Oxidation Protection

Ink materials, particularly conductive components, need to be protected against oxidation, especially in the case of easily oxidized metals such as copper and aluminum. Steric stabilizing agents used for aggregation protection can also provide an effective defense against oxidation. [64] These polymeric stabilizing agents surround the metal particles, providing protective barriers against both aggregation and oxidation. In addition to using polymeric materials to provide a steric barrier, antioxidants can also be added to the formulation to protect against oxidation. Antioxidants, such as ascorbic acid, have been shown to decrease the rate of oxidation of some metal nanoparticles. These methods of protecting against oxidation only slow down the process, instead of preventing it from happening. One way to completely prevent oxidation is to coat the nanoparticle with a substance that does not oxidize or whose oxidized surface still exhibits the desired functionality, such as silver. [64] Silver nanoparticles on their own are expensive, and therefore they are not as desirable, but less expensive metal nanoparticles such as copper and aluminum are subject to oxidation. However, coating a less expensive metal

nanoparticle such as copper with a silver coating can provide a less expensive option that is stable against oxidation. Silver-coated copper and other similar nanoparticles are gaining attention in the conductive ink industry.

Table 11. Additives Used in Printed Electronics Ink Formulations

Additive	Definition/Function
Dispersing agent	Prevent particles within the formulation from clumping together and forming aggregates; also referred to as aggregation protectant [307]
Antioxidant	Prevents the oxidation of components in the formulation [308]
Binder	Holds materials together to form a cohesive formulation [309]
Anti-foaming agent	Reduces and prevents the formation of foam during a liquid manufacturing process [310]
Drying agent	Induces or sustains a state of dryness in materials [311]; can also be used to increase the drying speed of inks [54]
Tack reducing agent	Reduces the tackiness of a formulation [312]
Curing agent	A catalytic or reactive agent that causes crosslinking of a material; also called a hardener [133]
Surfactant	Reduces the surface tension between two liquids; also called a wetting agent [133]
Rheology modifier	Used to control the rheology, or flow behavior, of a formulation [313]
Plasticizer	A material used in polymeric-based compositions that increases the workability and flexibility while decreasing the stiffness, brittleness, and viscosity of the formulation [133]
Anti set-off compound	Prevents the unwanted transfer of ink to any other part of the printing process, included other sheets of paper or equipment [314]
Waxes	Waxes can be added for a variety of functions, including to make the surface non-sticky (anti-blocking), to allow the surfaces to slide over one another (slip aid), to cause the formulation to be water resistant, and to alter the texture of the surface [315]
Shortening agent	Minimizes ink misting during printing [54]
Anti-skinning agent	Prevents the premature crosslinking of surface materials under the influence of oxygen [316]
Anti-pinholing compound	Reduces the number of small holes or voids in the print area [317]
Adhesion promoter	Increases the adhesion of the formulation to the desired substrate [318]
Humectant	Used to prolong the drying of the formulation; opposite of a drying agent [319]
Chelating agent	Ligands that form complexes with metal atoms to affect the solubility of a formulation [320]
Viscosity modifier	Adjusts and controls the viscosity of a formulation at various temperatures [321]
pH modifier	Maintains a desired pH value [322]

3.3.11. Ink Manufacturing

The processes used to manufacture printed electronics inks are very similar to traditional graphics/printing ink manufacturing methods, with the main difference being the material that is added to give the ink its functionality. Instead of using a pigment to impart an aesthetic functionality to the printing ink, a different functional component, such as a conductive particle,

is used to provide the ink with an electrical functionality. Essentially, an ink manufacturing process is simply a sophisticated mixing process. [323] While every ink manufacturer does things slightly different depending on the particular product they are making, there is a generally accepted generic method for manufacturing inks that most manufacturers use as a guideline for their processes. Some or all of the components of the formulation, which includes solvent, binder, and the functional component, are initially mixed together to form a pre-mix. The order of the mixing depends on several variables, including the viscosity and stability of the components and the compatibility of the components with each other. Typically, only a portion of the solvent is added in the pre-mix step because higher viscosity allows for better mixing. Once the desired consistency of the pre-mix is achieved, the remaining components, including the remaining solvent, are added if applicable, and mixing is continued to ensure that all of the components are dispersed to create a homogeneous mixture. Sometimes a milling or grinding step is required in order to reduce the size of the aggregates and evenly distribute the particulates.

Additives can be added at the end if necessary, to adjust variables such as viscosity and rheology. The general ink manufacturing process has a few challenges associated with it that ink manufacturers have to be aware of. First of all, it is difficult, but important, to ensure that the particulates within the ink formulation are ground down to the appropriate size, because if they are not, they can clog the ink dispensing units. Much care needs to be taken during the milling and mixing steps to ensure a homogenous mixture of properly sized particulates. Additives that control aggregation can also be added to help prevent the various particles from clumping together and causing clogged dispensing units. Another issue that ink manufactures tend to have is foaming, which results from the release of various gases, including air, that become trapped within the ink formulation. Fortunately, antifoaming agents can be added to prevent foaming and defoaming agents can be used to eliminate foaming once it occurs. These additives help to penetrate the liquid-air interface in the foam and slow foam formation. In addition to the above challenges, manufacturing inks specifically for printed electronics applications requires a few more considerations. GEM, mentioned in the conductive inks section (3.3.3), released a presentation describing their development of conductive inks and the various concerns it is necessary to be aware of for conductive ink manufacturing. [324]

Gwent mentions that while it is desirable to combine solvents in order to obtain the best possible drying properties, it is important to be aware throughout the mixing process of the boiling points and evaporation rates of the different solvent systems that are being used. The solvents used will also often dictate what resin system can be used because not all resins will be soluble in all solvents. The resin chemistry and how much the material shrinks as it dries or swells as it absorbs solvent will have a direct effect on the electrical functionality of the dried ink and the manufacturability of the ink. The particles of the functional components and additives will have an effect on the rheology of the ink, which in turn dictates ease of mixing and printability. Therefore, it is important to consider particle size, particle size distribution, and particle surface area for any particulate component in the formulation. Functional particles have a tendency to agglomerate, and coatings are often used to isolate each particle and prevent this aggregation.

However, the solvents chosen for the ink must be capable of removing the protective coating at the appropriate time in order to enhance the conductivity of the system. Overall, while designing

an ink formulation is not simple at all, ink manufacturing is a relatively simplistic process, especially compared to other manufacturing processes, such as the printing techniques that are used to deposit inks. As described above, there are challenges associated with ink manufacturing, and many solutions to these problems have already been found through various additives, but some of the existing problems will need to be addressed as FHE become more prevalent.

3.3.12. FHE Materials Market

Table 12 below provides a snapshot into the companies identified, as of December 2015, that are involved in the FHE ink/deposition materials industry.

Table 12. FHE Ink/Materials Companies

	Company	Headquarters	U.S. Location	Product
1	C3Nano	California	California	solution coated transparent conductive materials to replace ITO, carbon-based materials
2	Mitsubishi Imaging (MPM), Inc	New York	New York	silver nano ink and inkjet media that chemically sinter at room temperature
3	Agfa-Gevaert	Belgium	South Carolina	inkjet inks, conductive silver ink
4	Seiko-Epson	Japan	California	semiconductor materials
5	T-ink	New York	New York	conductive inks
6	Allied PhotoChemical	Michigan	Michigan	colored & clear UV coatings, dielectrics & encapsulants, silver & nano conductive inks, allied photopolymers, EL formulations
7	Engineered Conductive Materials	Ohio	Ohio	silver inks, conductive inks, carbon inks, dielectric, epoxy, insulator
8	Next Energy Technologies	California	California	organic semiconducting inks
9	FlexTech Alliance	California	California	collaboration, support, consulting for flexible printed electronics industry
10	Palo Alto Research Center (PARC)	California	California	materials characterization
11	Nantero	Massachusetts	Massachusetts	microelectronic grade CNT coating
12	Creative Materials	Massachusetts	Massachusetts	silver inks, carbon inks, dielectric inks, conductive adhesives
13	Epoxy Technology	Massachusetts	Massachusetts	conductive epoxies
14	XG Sciences	Michigan	Michigan	GNPs, graphene inks, graphene coatings, conductive inks, graphene sheets
15	Conductive Compounds	New Hampshire	New Hampshire	carbon inks, conductive epoxies, metal inks, dielectric inks
16	Liquid X Printed Metals	Pennsylvania	Pennsylvania	functional metallic inks
17	Intrinsiq Materials	New York	New York	copper inkjet ink, copper screen paste, nickel inkjet ink, nickel silicide, silicon ink
18	Cambrios	California	California	silver NW formulations

Table 12. FHE Ink/Materials Companies (cont'd)

	Company	Headquarters	U.S. Location	Product
19	Seashell Technologies	California	California	silver NWs, nanospheres, nanoplasmon
20	Graphene Technologies	California	California	graphene, graphene inks, nanomaterials, magnesium oxide
21	Methode Electronics	Illinois	Illinois	conductive inks, resistive inks, silver inks, carbon inks
22	Ercon	Massachusetts	Massachusetts	silver chloride inks, graphite inks, platinum gold catalyst inks, protective insulating coatings, silver inks, epoxies, carbon inks
23	Vorbeck Materials	Maryland	Maryland	graphene-based conductive ink for screen, flexo, gravure printing
24	ULVAC	Massachusetts	Massachusetts	silver inks, gold inks, ITO inks
25	Brewer Science	Missouri	Missouri	CNT inks
26	Protavic America	New Hampshire	New Hampshire	conductive adhesive, non-conductive adhesive, encapsulation resin, potting resin, sealants, coatings, electrically conductive inks/paints
27	Universal Display Corporation	New Jersey	New Jersey	OLED materials, phosphorescent materials,
28	Sun Chemical Corporation	New Jersey	New Jersey	conductive inks, resists, solder mask, dielectric, insulators, inkjet inks
29	SWeNT	Oklahoma	Oklahoma	SWCNTs, conductive CNT ink, semiconducting CNT ink
30	NovaCentrix	Texas	Texas	nanopowders, nanoaluminum, and nanosilver
31	Applied Nanotech	Texas	Texas	conductive inks, conductive pastes, CNTs, nanoparticles, graphene films
32	Xymox Technologies	Wisconsin	Wisconsin	conductive silver ink, clear encapsulants, conductive epoxy
33	Micro Chem Corporation	Massachusetts	Massachusetts	photoresists, dyes, epoxy, dielectrics, polymers
34	PChem Associates	Texas	Texas	silver nanoparticle conductive inks
35	Harima Chemicals	Japan	Georgia	metal pastes, metal nanoparticle pastes
36	Johnson Matthey	Netherlands	Pennsylvania	silver powers, silver flakes, printed electronics inks, passive component inks, silver salts, specialty silver materials, PV, silver inks
37	SOLVAY Organic Electronics	Brussels	locations all over US	specialty polymers, organic polymers
38	DuPont Microcircuit Materials (MCM)	Delaware	locations all over US	conductive inks, hybrid circuit materials, LED lighting materials, passive component materials
39	BASF New Business	Germany	locations all over US	organic semiconductor materials, isolators, phosphorescent light emitting materials
40	iimak	New York	New York	conductive thermal transfer ribbons, conductive inks for screen & flexo
41	ELANTAS	Germany	Missouri	primary insulation, secondary insulation

Table 12. FHE Ink/Materials Companies (cont'd)

	Company	Headquarters	U.S. Location	Product
42	Sigma-Aldrich / Sigma-Aldrich Fine Chemicals (SAFC) Hitech	Missouri	Massachusetts	LED materials, semiconductor materials, energy and display materials
43	AZ Electronic Materials	Luxembourg	New Jersey	lithography technology, photoresists, solvents, adhesion promoter, silicon technology, dielectrics, resins, coatings
44	Taiyo America	Nevada	Nevada	solder masks, etch, resist, silver conductive paste, liquid dielectric, conductive paste
45	IDTechEx	United Kingdom	Massachusetts	materials for printed, flexible, organic electronics
46	Gwent Group (Gwent Electronic Materials)	United Kingdom	California	inks, metal complex inks, metallorganics, pastes, graphene
47	Heraeus	Germany	New York	Clevios technology - conductive, transparent, and flexible polymers
48	Ricoh	Japan	Pennsylvania	organic semiconductor polymer
49	Henkel	Germany	Connecticut	adhesives for electronics and semiconductor assembly, chip-on- board (COB) encapsulants, conductive adhesives, display materials, solder materials, thermal management materials, underfill materials, printed electronics materials, conductive inks, silver inks, resistive inks, carbon inks, dielectric inks
50	The Merck Group (EMD Performance Materials)	Germany	Massachusetts	Small molecules and soluble systems, printable polymers
51	Plextronics	Pennsylvania	Pennsylvania	electronic inks, conductive inks, electronic polymers, conductive polymers
52	Nano-C	Massachusetts	Massachusetts	fullerenes, fullerene derivatives, CNTs
55	Raymor Industries	Canada	No	metallic nanotubes, semiconducting nanotubes, plasma nanotubes, graphene platelets
53	Polyera Corporation	Illinois	Illinois	semiconductor inks, dielectric inks, interface materials, functional ink, transistor inks
54	Eikos	Massachusetts	Massachusetts	Nanotube inks, binder inks
56	Sheldahl, Inc	Minnesota	Minnesota	thin film coatings, specialty gold coated materials, splicing tapes, electronic materials, adhesives, tapes, shielding materials, optical materials, flexible substrates and laminates, thin films, coated films, patterned films
57	Voxel8, Inc.	Massachusetts	Massachusetts	inks for a 3D electronics printer for additive manufacturing of parts with electronic devices and capabilities inside; silver ink, advanced matrix materials, functional inks

Table 12. FHE Ink/Materials Companies (cont'd)

	Company	Headquarters	U.S. Location	Product
58	Engineered Material Systems, Inc. (EMS)	Ohio	Ohio	Adhesives, encapsulants, silver inks, carbon inks, dielectrics, conductive inks, resistive inks
59	Meliorum Technologies, Inc.	New York	New York	silicon nanoparticles, silicon nanoparticle inks, gold nanoparticles, zinc oxide nanoparticles, semiconductor inks, metal oxide nanoparticles, binary semiconductor nanoparticles
60	NanoGram Corporation	California	California	inorganic nanomaterials, coatings, films, silicon inks, silicon nanoparticles, silicon nanoparticle inks
61	Nth Degree Technologies	Arizona	Arizona	Inorganic semiconductor inks
62	Inkron	Hong Kong	None	Die attach pastes, conductive inks, conductive pastes, dielectrics, encapsulants, nanopowders
63	Degussa Corporation	Ohio	Ohio	Metallic nanoparticles
64	Nanograde	Switzerland	None	Specialty inorganic nanoparticles
65	PV Nanocell	Israel	None	Conductive silver and copper inks
66	Genes' Ink	France	None	Conductive inks, semiconducting inks, silver inks
67	Kunshan Hisense Electronics Co	China	None	Silver conductive ink, inkjet inks, conductive silver paste, dielectric ink
68	InkTec	Korea	None	Metal complex inks
69	Haydale	United Kingdom	None	Graphene-based inks, functionalized CNTs
70	Caledon Controls	Canada	None	Dielectric inks, conductive inks, UV curable inks, thermally cured inks, EL inks

TECHNOLOGY GAP: INKS/DEPOSITION MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

There is often a trade-off between high performing, rigid, inorganic materials and lower performing, flexible, organic materials for electronics, particularly FHE.

POTENTIAL SOLUTION

The designer has to determine which is best for the desired end use and application of the device. Additionally, the opportunity exists for increasing the performance levels of organic materials and/or increasing the flexibility of high performance inorganic materials.

TECHNOLOGY GAP: INKS/DEPOSITION MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

The high post-processing temperatures necessary to enhance the performance of various ink formulations poses problems for the manufacturing of flexible electronics devices.

POTENTIAL SOLUTION

Increasing the heat resistance of various flexible substrates that are used in the design of FHE, as well as developing alternative, low-temperature, post-processing methods will help to eliminate this technology gap.

TECHNOLOGY GAP: INKS/DEPOSITION MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

Silver, one of the most commonly used materials for conductive formulations, allows for some of the highest performance levels in the industry, but unfortunately also significantly increases the price of conductive inks.

POTENTIAL SOLUTION

Ink developers can attempt to improve the quality and performance of their inks so less silver has to be incorporated into the formulation, or so less ink needs to be used overall. Less expensive silver substitutes, such as silver coated copper nanoparticles, are being investigated, as well.

TECHNOLOGY GAP: INKS/DEPOSITION MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

Today's CNT materials are produced as a mixture of conducting and semiconducting forms, which poses potential problems when pure forms of CNT materials are needed, since purification can be a time consuming and difficult production step. This leads to CNT devices sometimes having a tradeoff between mobility and on/off ratio.

POTENTIAL SOLUTION

Various companies and research organizations are investigating methods for separating and purifying CNT materials, which includes two phase extraction based on chiral separation principles. However, further research is needed in this area, especially with regards to stabilizing the CNT products after purification.

TECHNOLOGY GAP: INKS/DEPOSITION MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

Due to the relatively new nature of this industry, materials often have batch-to-batch inconsistencies, which leads to problems regarding characterization and qualification of materials for use in bulk manufacturing.

POTENTIAL SOLUTION

The FHE industry needs to come together, perhaps through the FHE Manufacturing Innovation Institute, to identify materials of promise and solicit help from industry and academia to develop new ISO-type handbooks for FHE materials.

3.4 Substrates for Printed Electronics

As defined previously, FHE refers to devices, systems, and processes that combine conventional rigid inorganic semiconductor technologies with innovative features, such as organic materials, mechanically flexible substrates, and/or functional printing techniques. In conventional electronics, the substrate is typically a rigid wafer or PCB. As electronics move from conventional to FHE technologies, the substrates used for electronics are becoming less rigid and more mechanically flexible, and in fact, flexible thin films of various materials are becoming very popular as substrate materials.

Several different substrate materials have been investigated for use in FHE technologies, including several types of plastic, paper, ceramic, glass, and others like fabrics and metal foils. But no matter which one is selected, the performance characteristics of the substrate will always impact the application. [325] Therefore, many factors have to be considered when selecting a substrate, including ink adhesion, surface roughness, material behavior over time, heat treatment, humidity behavior, the effect of being in a roll format, and lamination. Additionally, since webs are under tension in a roll-to-roll manufacturing environment, it is important to know the tensile strength of the substrate material, whether or not it stretches under tension, and how it behaves mechanically under heat and humidity changes. Since there are so many important variables to consider when picking a substrate material for a FHE application, there may not be one substrate for all applications, but rather a gold standard substrate for specific applications depending on device and manufacturing needs.

In this section, four of the most prominent substrates used for FHE, ceramic, paper, plastic, and glass, are described in detail. It is important to stress, though, that these four materials do not comprise the entirety of the FHE substrate market. Fabrics are used predominantly for wearable applications, and metal foils are often substrates for displays and photovoltaic technologies.

However, since wearables, displays, and photovoltaics were not emphasized as FHE applications in this report, fabric and metal foil substrates are not discussed in detail in this section.

Table 13 provides a brief summary of key relevant material properties for the substrates found in the subsequent sections.

Table 13. Property Comparison for FHE Substrate Materials [326] [327] [328]

Substrate	PEN	PET	Ceramic	Flexible Glass	Paper
Transparency	87%	90%	translucent	> 90%	88 – 90%
Drawback	High CTE	Process Temp	Not Foldable	Brittle	Surface Roughness
Tg	180 °C	80 °C	Unknown	600 °C	200-250 °C
Cost	Midrange	Low	Midrange	High	Very Low
Surface Roughness	15 nm RMS	15 nm RMS	20 – 25 nm RMS	0.5 nm RMS	1.07 – 232 nm RMS

3.4.1 Ceramic

Thin films of ceramic material are being used as substrates for flexible electronics. There are many characteristics that make ceramic an appealing substrate choice. [327] First of all, ceramic substrates are robust but lightweight materials, allowing the possibility of integrating electronics into a structure without adding too much weight or losing integrity. Secondly, ceramic is an extremely inert and dense material, and therefore it displays no out gassing nor does it let impurities or humidity to be absorbed, minimizing the possibility of contaminants that could decrease electrical performance. Low surface roughness (20-25 nm) can be achieved with ceramic substrates, ensuring a more even distribution of ink materials. Typically, ceramics are opaque, but translucent properties have also been achieved, which allows for both sides of the substrate to be printed with adequate resolution. Finally, thin ceramic has very good dielectric strength, which is a very desirable property for substrates used in electronics.

Ceramic substrates can be easily coated by various processes to enable different attributes. [327] For example, high quality ceramic substrates can be achieved by depositing high temperature thin films on the substrate surface. Processes such as these enable the operational temperature to range from -150° C to 1000° C, and short term processing temperatures can be even higher. Additionally, not only can they withstand operating at these extreme temperatures, but they have thermal shock tolerance as well. Thin ceramic substrates can withstand changing from subzero temperatures to extremely hot environments within seconds, without losing flexibility. Their low thermal mass provides for rapid heat loss, which is ideal for highly integrated electronics packages which sometimes have thermal management and heat dissipation issues. Unfortunately, there are disadvantages to this technology as well. Although the ceramic substrate is highly flexible, it is not foldable. [327] Ceramic substrates will break if folded in two, unlike paper and plastic substrates. Overall, all these properties together align ceramic substrates with many FHE applications, such as wearable electronics, mechanical sensors, medical electronics, micro batteries, solar photovoltaic, power electronics, solid state lighting, transparent infrared windows, fuel cells, superconductors, flexible heaters, embedded heaters, actuators, piezoelectrics, and sensors (optical, vibration, mechanical, cryogenic). [327]

One company that is pioneering new properties in thin film ceramic substrates for printed electronics is ENrG, a public company founded in 2003 and located in Buffalo, NY. [327] EnrG currently offers two products, Thin E-Strate® and Ultra-Thin E-Strate™, which are thin, flexible ceramic substrates with thicknesses of 40µm and 20µm, respectively. Both products are offered as coupons, sheets, wafers, and short strips. ENrG's substrates can be used for several

applications, including wearables, sensors, and photovoltaics, among others, but unfortunately this ceramic product is not a good candidate for high frequency usage (above 20 Hz). ENrG was working to develop a copper laminated ceramic substrate for use with flexible and thinner circuit boards. Their website says prototypes of this technology would be available by the end of 2014, but no further information could be found. Other innovations include development of their thin ceramic substrates for a roll-to-roll format, which is projected to be released in 2016.

Another large U.S.-based company producing thin film ceramic substrates is CoorsTek, headquartered in Golden, Colorado. CoorsTek has their own line of flexible thin film ceramic substrates with properties that are desirable for the FHE market. The surface roughness and density of the material is comparable to ENrG's products, but the CoorsTek products are not translucent and are only offered in white. One advantage of CoorsTek products are they are good for high frequency applications. Currently, CoorsTek products are only offered in sheets and wafers. A few examples can be found of researchers using both of these companies' technologies to create FHE. In 2014, researchers from the U.S. Photovoltaic Manufacturing Consortium, SUNY College of Nanoscale Science and Engineering, and ENrG published a paper detailing their experiments using ENrG's Thin E-Strate® technology to create thin film copper indium gallium diselenide solar cells. [329] The researchers identified that the flexibility, smooth surface, lack of impurities, and roll-to-roll compatibility of Thin E-Strate® is what made it the ideal substrate for their application. Their small area solar cells fabricated on ENrG's substrate yielded a 17.3% efficient device.

Additionally, researchers from Arizona State University and University of California San Diego used a thin ceramic substrate from CoorsTek, along with three other plastic film substrates, to study the impact of mechanical bending and stress on the electrochemical behavior of flexible thick-film electrochemical sensors. [330] Overall, ceramic materials are probably the least popular substrate for flexible electronics out of the four mentioned here. However, with new innovations like ENrG's technology, especially with its roll-to-roll compatible format expected release in 2016, it is not unanticipated that ceramic substrates will start to play a larger role in the FHE industry.

3.4.2 Paper

Paper has been manufactured and produced in a roll-to-roll process for over a century, and research involving the use of paper substrates for electronics dates back approximately 50 years. Paper is cheaply manufactured and highly flexible and foldable, making it an extremely desirable substrate, especially because paper is manufactured from renewable raw materials, and is disposable, biodegradable, and recyclable. Additionally, paper has about 100,000 times the intrinsic resistivity of silicon, so in theory it almost completely eliminates the chance of electrons undesirably traveling through the substrate. [328] The two main challenges for paper as a substrate for electronics are surface roughness and humidity effects. [328]

Paper is simply a pressed mat of cellulose microfibers, which equates to an extremely rough surface texture. [331] Therefore, in order to be used in electronics applications where a low surface roughness is typically ideal, a coating needs to be applied to the paper surface. This coatings can be a mixture of pigments, binders, and process materials, all designed to smooth the intrinsically rough surface of the paper. With these coating and processing methods, specially

designed electronic papers can approach to the surface roughness of glass substrates; they can reach approximately 1 nm – original copier paper has a surface roughness of 118 nm while the value for LCD glass is 0.42 nm. These coatings also help to seal the paper in order to prevent water and other solvents being absorbed into it. These challenges can also be mitigated through calendaring the paper during the manufacturing process (calendaring refers to using hard pressure rollers to smooth a sheet of material). [328]

Another challenge associated with paper is porosity, but this can also be attenuated by the type of coatings that are applied to the paper before the application of inks. For FHE applications, fine patterning as low as 5 microns on paper substrates has been achieved. Paper has been investigated for use in sensors, RFID tags, printed batteries, transistors, pixels/displays, and microfluidics. Both inorganic materials, such as silicon or indium gallium zinc oxide, and organic materials, such as pentacene or poly(3-hexylthiophene) (P3HT), have been used for the current carrying channels in paper-based transistors, but overall organic semiconductors seem like the better choice for mass production. [328] While organic transistors tend to be slower due to the intrinsic properties of organic materials, organic compounds can be dissolved in fluid and deposited on paper using roll-to-roll printers, and they have a higher sensitivity to environmental conditions. Additionally, because paper would essentially combust at the temperatures used to grow crystalline films used in traditional semiconductors, inorganic paper-based transistors are typically made from amorphous, noncrystalline films that can be formed at a lower temperature through evaporation or sputtering.

As of 2013, about a half dozen research groups have made considerable headway in constructing paper-based transistors. [328] John Rogers' group at the University of Illinois at Urbana-Champaign is one of these, and they have been working to create circuits on silicon and then transfer them to paper. This approach, while unfortunately being more costly, typically leads to better performing circuits. A research group at Linköping University in Sweden pioneered electrochromic display applications for paper-based electronics. [328] Their display uses conducting polymer pixels, and under an appropriate voltage, the polymer changes color.

Andrew Steckl's group at the University of Cincinnati has an alternative display technology called electrowetting, which is a technique typically used with glass. This approach involves confining colored liquids between two surfaces and altering their surface tension using an applied voltage, which either allows the colored liquid to spread out and reflect light or ball up and allow light to pass through. Microfluidics, which involves transporting liquids from one spot to another, is an application for paper-based electronics that actually works with paper's intrinsic properties. [328] The narrow channels between fibers in paper excel at drawing in water and other fluids by capillary action.

Medical testing devices are one of the main markets for this kind of technology, such as microfluidic paper-based systems that could monitor liver function or diagnose tuberculosis, and researchers at both Harvard University and the University of Washington are heavily invested in this area. In fact, this paper-based medical testing device technology has already lead to spin-off companies, suggesting that medical diagnostics will probably be the first paper-based technology to be commercialized. At the Chinese Academy of Science in Beijing, Jing Liu and his team have successfully printed electronics on paper. Jing's team printed circuits and other functional

components on paper, including conductive wires, inductance coils, and flexible antennas. They used a combination of liquid ink and rubber printed in channels that allowed the ink to dry in place on the paper. [332]

Various types of previously existing paper products can be used for electronics applications, such as wax-coated paper, standard smooth finish commercial papers, and translucent papers called glassine. [328] Alternately, some papers have actually been designed specifically for electronics substrates. Sappi Fine Paper North America, located in Boston, created a polymer-coated paper with an average surface roughness of just a couple nanometers, which is only slightly more than glass substrates. Additionally, in December 2012, Arjowiggins Creative Papers, located in France, unveiled Powercoat®, which is a paper substrate designed specifically for electronics applications. [333] This product has incredible smoothness (as low as 10 microns), is roll-to-roll compatible, allows for fine patterning as low as five microns, is completely recyclable and biodegradable, and can withstand the high temperatures required for low resistance silver ink without the discoloration experienced by other papers on the market. Arjowiggins' product is ideal for sensors, RFID tags, and printed batteries, among others.

Despite paper being created specifically for electronics applications, the exact type paper used in any particular electronics technology will heavily depend on the desired function and end application because of the large range in properties between the different types of electronics paper available. Overall, paper is most likely going to be influential in markets where low cost is the main objective. [328] Unfortunately, plastic substrates are more rugged and electronics-friendly, and glass is becoming thin enough to be flexible, but it is likely that paper-based electronics will find their niche in the overall FHE market, particularly in the specific applications mentioned above.

3.4.3 Plastic

Polymers are widely used in the microelectronics industry for a variety of reasons, including their relatively low cost, and those same reasons make them attractive materials for FHE substrates as well. There are many different types of plastics and polymers that are used as substrates for flexible electronics, including PI, PET, and PEN. Plastic substrates are extremely desirable from a mechanical flexibility standpoint, but other characteristics of plastic are not as comparable to conventional substrates, such as glass. "To replace glass, however, a plastic substrate needs to be able to offer some or all of the properties of glass, i.e., clarity, dimensional stability, thermal stability, barrier, solvent resistance, and low coefficient of thermal expansion (CTE) coupled with a smooth surface." [334] Additional desired qualities for roll-to-roll plastic substrates include high mechanical strength, low water absorption, excellent dielectric properties, and good thermal resistance in terms of shrinkage and degradation of the polymer chains.

Since no plastic material exists that possess all of the same characteristics as glass, a composite, multilayer substrate structure might be needed to achieve all of these qualities. Alternately, substances can be introduced to the polymer or processing can be used to alter material properties, such as the surface smoothness and opacity of the film, in order to impart some of these desired qualities. High temperature stability is probably the most widely recognized downfall of plastic substrates for FHE, but manufacturing processes can be used to increase the thermal resistance of some substrates. [334] For example, PET and PEN films (Melinex and

Teonex both produced by DuPont Teijin Films) are manufactured using a series of stretching techniques which stretch the polymer biaxially (in both the machine and traverse direction) and then heat set the material at an elevated temperature. A semicrystalline microstructure results that is stiff, strong, and thermally stable, but unfortunately the increased thermal stability can come at the expense of reduced flexibility and transparency. When exposed to additional heat over a period of time, the PET and PEN films become heat stabilized and can withstand even higher processing temperatures. Table 14 demonstrates this fact and also provides a comparison of plastic substrates with respect to several variables that are important to FHE applications.

In addition to thermal stability issues, polymers also have high permeability characteristics, which can lead to device reliability issues resulting from high WVTRs and oxidation. [335] Often, barrier layers, such as thin layers of aluminum or oxides, can be applied using traditional deposition methods to reduce the permeability of these polymer substrates. [336] Additionally, polytetrafluoroethylene (PTFE) has been used in microelectronics as an outer coating for devices. [337, 338] It is resistant to chemicals and wear, and has a melting temperature of approximately 350 °C, which allows it to be used in processing environments up to 250 °C. [339] Indications of permeability rankings for several plastic substrates are also included in Table 14.

Table 14. Comparison of Key Properties Relevant to Flexible Electronics [334]

√√√ Excellent √√ Good √ Moderate X Poor	Substrate					
Property	**Heat-stabilized PEN Teonex® Q65**	**Heat-stabilized PET Melinex® ST504/506**	**PC**	**PES**	**Polyarylate**	**Polyimide**
CTE (-55 – 85 °C) (ppm/°C)	√√	√√	√	√	√	√√
%Transmission (400 – 700 nm)	√√	√√	√√√	√√	√√	X
Water absorption (%)	√√	√√	√	X	√	X
Young's modulus (GPa)	√√	√√	√	√	√	√
Tensile strength (MPa)	√√	√√	√	√	√	√
Solvent resistance	√√	√√	X	X	X	√√
Upper operating temperature	√√	√	√	√√	√√√	√√√

PET and PEN films are probably the two most widely used plastic film substrates for FHE, but other materials can be used as well, including polycarbonate (PC), polyethersulphone (PES), polyarylate (PAR), and polyimide, as seen above in Table 14. [334] There are three different categories of plastic films: semi-crystalline (e.g. PET, PEN), amorphous (e.g. PC, PES), and solvent cast amorphous (e.g. fluorene polyester, PI). These broad classifications are based on the glass transition temperature of the film substrates. Since plastic films are used for a large number

of industries outside of electronics, countless companies exist that produce these kinds of films. DuPont Teijin Films (Delaware), Coveme Spa (Italy), Eastman Kodak Company (New York), Sabic (headquarters in Saudi Arabia with wholly owned subsidiary in Texas), Ferrania Technologies (Italy), and others are just a few examples of companies that produce films that fall within the three classifications mentioned above (semicrystalline, amorphous, and solvent cast amorphous). [334]

As mentioned above, DuPont Teijin Film produces Melinex and Teonex, which are semicrystalline PET and PEN films, respectively. A few examples of solvent cast amorphous materials include DuPont's Kapton polyimide film and Ferrania Chemicals' AryLite aromatic fluorene containing PAR film. Teijin's Pure-Ace® and Sabic's Lexan™ are examples of amorphous polycarbonates. Out of all of these film manufacturers, DuPont Teijin Films is probably the most commonly used and well recognized brand of plastic film substrates for FHE applications. As a whole, DuPont's polyester film technology (PET, PEN) is characterized by high stiffness, dimensional stability, optical transparency, and solvent resistance. [340] The films are semicrystalline, biaxially oriented, and range in thickness from 0.6 – 500 µm. The films are subjected to a heat stabilization process, and off-line stabilization is typically required for electronics applications in order to reduce film shrinkage. DuPont has several recent film developments that are applicable to flexible electronics, including enabling clean and smooth film surfaces. [340] Having a smooth film surface is a necessary characteristic for many industries, and it is particularly important in flexible electronics. Traditionally, to address this issue, off-line, planarized film coatings were applied on top of the plastic film. This coating would cover all of the surface defects on the film, such as pinholes, dust, and catalyst residue. This method is effective, but since it is off-line, it adds a significant cost to the process.

Clean-On-Demand is a new surface smoothing method being developed through the European Clean4Yield project. This method involves coextruding a sacrificial protective film along with the plastic film. The sacrificial layer absorbs all of the damage and defects associated with subsequent web transport handling, and then is peeled off when the plastic substrate is about to be used. This technology is still in development at DuPont, but potentially could provide an option for decreasing surface roughness for plastic films in the future. Similar to the large amount of plastic film companies that could be identified, endless examples exist of universities using plastic substrates for FHE research. A brief sampling of these examples is subsequently provided.

In 2004, researchers from Tokyo Institute of Technology published a paper describing their work to fabricate transparent flexible thin-film transistors at room temperature conditions. [341] To achieve this, they deposited amorphous oxide semiconductors onto PET substrates to achieve saturation mobilities of 6 – 9 cm2/Vs and stable device performance during repetitive bending cycles. A year later, researchers from Harvard University published their work to create high-performance electronics and photonics on flexible plastic substrates. [342] Specifically, they were creating FETs and light emitting diodes with nanoimprint lithography techniques and successfully fabricated silicon NW FETs that displayed mobilities of 200 cm2/Vs. In 2007, a team from Georgia Institute of Technology described their efforts to create nanowire piezoelectric nanogenerators on plastic substrates. [343] Their technology can successfully function as a flexible power source and has potential applications in nanodevices, including

implantable biosensors/biodetection devices, wireless self-powered sensors, and self-powering electronic devices.

A research team from Purdue University, Northwestern University, and University of Southern California also published their FHE work utilizing plastic substrates in 2007. [344] This group was able to develop fully transparent nanowire transistors on flexible plastic substrates for use in AMOLED displays. It appears that the FHE industry as a whole is focusing mainly on plastic films for substrates, as demonstrated by the large amount of companies and universities that are active in this area. As long as steps continue to be taken to address the high temperature issues associated with plastic film substrates, it is likely that this substrate will continue to be the frontrunner for the near future, due to its roll-to-roll compatibility, flexibility/foldability, ruggedness, transparency, and relatively high strength and humidity resistance as compared to other thin film substrates.

3.4.4 Glass

Glass has traditionally been used as a substrate for conventional rigid electronics because of its clarity, dimensional stability, thermal stability, barrier properties, solvent resistance, low CTE, and smooth surface. [334] Overall, as a substrate, glass offers improved resolution, registration, performance, and lifetime over other substrates. [345] Glass fared much better than any plastic product when exposed to prolonged heat and humidity levels. In particular, it could handle temperatures as high as 200 °C and be exposed to relative humidity of 85% at 85 °C for two days without significant negative effects. In both environments, the glass proved to have high dimensional stability. However, glass can be costly and has a tendency to break if not handled properly during the manufacturing processes. Thin, flexible glass has become a reality and an increasingly popular substrate choice for FHE.

Corning, headquartered in Corning, NY, has become a pioneer in this area. They developed Willow® Glass, a flexible glass substrate that is compatible in both a sheet-fed and a roll-to-roll processing environment. It has a thickness of 200 microns or less, which is much thinner than other typical glass substrates that have thicknesses of 0.2-0.5 mm. [346] Flexible glass substrates offer some of the advantages of conventional rigid glass substrates, but they also have some benefits of their own. These advantages include optical quality, surface quality, thermal capability/stability, dimensional stability, chemical compatibility, and hermeticity. [347] Willow® Glass was developed to serve as both a device substrate and for hermetic barrier applications. Because of the few disadvantages mentioned above, glass will not be a wise choice for all applications, but Corning's Willow® Glass is formulated to perform exceptionally well for electronic components such as touch sensors, and as a seal for OLED displays and other moisture and oxygen sensitive technologies. [348] To improve on its current technology, Corning is focusing on the mechanical reliability of Willow® Glass, which involves controlling defects and applied stresses in the manufacturing environment through appropriately monitored handling and conveying processes.

Organizations currently using Corning's Willow® Glass technology include the Center for Advanced Manufacturing (CAMM) at Binghamton University, Frontier Industrial Technology, Inc. (Pennsylvania), and ITRI (Taiwan). Other ultra-thin glass manufacturers outside of Corning include Nippon Electric Glass Co., Ltd. (Japan), Asahi Glass Co., Ltd. (Japan), and Schott (New

York). [347] Since the launch of Corning Willow® Glass in 2012, multiple examples of researchers utilizing this substrate technology can be found throughout literature. In 2013, researchers from Spain released a paper documenting their work to create highly transparent conductive films on flexible glass substrates. [349] In order to achieve this, they hot-pressed graphene onto a silver nanowire mesh that was located on the flexible glass substrate.

In the same year, a team from Georgia Institute of Technology used flexible glass substrates to create stacked inverted top-emitting green electrophosphorescent OLEDs. [350] A year later, researchers from the National Renewable Energy Laboratory in Colorado described their use of flexible glass as a substrate for thin film photovoltaics. [351] Additionally, in 2014, the University of Cincinnati and AFRL worked together to create pentacene organic thin-film transistors on flexible glass substrates. [352] Overall, it appears that since the release of Corning's Willow® Glass, there has been an explosion of research regarding flexible glass substrates for FHE applications. This observation is not surprising due to the fact that glass has been an ideal substrate in the conventional electronics market for decades. While flexible glass is definitely not as mechanically flexible and foldable as other substrates like plastic and paper, it has a long list of properties that are desirable for electronics applications, and it can only be expected that it will continue to be researched as a potential substrate for FHE.

TECHNOLOGY GAP: SUBSTRATE MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

As single-use and disposable electronic devices become ubiquitous, plastic substrates may become too costly, and they also may not meet certain operating condition requirements, such as extreme temperature stability.

POTENTIAL SOLUTION

Other material options, such as thin, flexible ceramic and glass, can meet the extreme operating condition requirements, but further research will have to be performed in order to decrease the cost of these relatively new materials.

TECHNOLOGY GAP: SUBSTRATE MATERIALS FOR FLEXIBLE HYBRID ELECTRONICS

Unlike traditional rigid electronics, most FHE devices are not manufactured in a clean room, which means that many of the roll-to-roll flexible substrate surfaces are contaminated with impurities.

POTENTIAL SOLUTION

Substrates will have to endure a web cleaning pretreatment, but further research will need to be performed to create domestic capabilities for this process.

4.0 MANUFACTURING TECHNOLOGY FOR FLEXIBLE HYBRID ELECTRONICS

Conventional electronics have been made the same way for decades - on silicon wafers utilizing photolithographic techniques. Unfortunately, this manufacturing process is wasteful and costly since more product is etched away from the silicon wafer than remains. New techniques for manufacturing electronics are being developed by companies and universities all around the world, creating a market that is being referred to as flexible hybrid electronics (FHE).

Techniques borrowed from the paper and printing industries are being adapted to print electronics or parts of electronics on to substrates that include everything from paper to ceramic. As a parallel track to the printing technologies, conventional processing methods are being adapted to be additive and not subtractive, and such techniques have actually been able to make silicon flexible. Instead of looking for a "one size fits all" approach that can be used for all types of electronics, the different manufacturing processes, including the ones mentioned above, will most likely be adapted to meet the needs of the specific end use application. Several of these manufacturing methods for FHE, including their advantages, disadvantages, and the various applications they are well-suited for, will be described in the subsequent paragraphs.

4.1 Manufacturing FHE with Innovative Manufacturing Technologies

Roll-to-roll manufacturing is a method that has been used in the paper making and printing industries for centuries. During the process, a substrate material is unwound from a parent roll and through a predetermined set of stages to allow the materials to be printed onto the substrate. Stages include pre-treatment, printing (gravure, lithography, flexography, inkjet, offset, screen), coating, drying, curing and calendaring. The type of printing that is used is highly dependent on the materials being utilized, both ink and substrate, and the type of flexible electronics that are being produced. The configuration of the printing machine is also variable based on the product being produced. Processes may become more concrete as the industry standards start to take shape.

There are various advantages to printing electronics in a roll-to-roll production set up, with cost being the most significant factor. The capital cost requirements to set up a silicon facility can be several billion dollars. Establishing a startup printed electronics facility would cost 1/100th of the cost of a traditional silicon facility. [353] Printing electronics is more economical than the traditional silicon method due to the additive way the materials are used. The inks and coatings are placed exactly where they are needed. In traditional silicon photolithography methods, materials are applied uniformly and then unneeded/unwanted materials are etched away. The waste component can be seen not only as an economic impact but also an environmental impact. In conventional electronics, 70% of the cost is associated with integration and assembly. Printed electronics, on the other hand, are innately more integrated, and this technology has the ability to print several functional elements at the same time with the same material, ultimately saving cost. Time, economics, and start-up costs are driving the electronics market toward printed electronics, and as printing technologies improve, more devices will be produced this way.

4.1.1 Pre-Processing Methods

Pretreatments are an important step for the adhesion of inks to substrates. Pretreatments, such as plasma and corona treatment, have the ability to change the properties of the surface of a

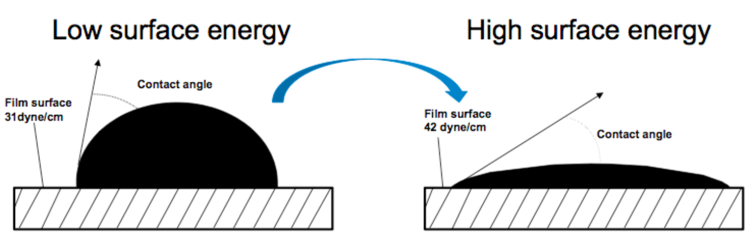
substrate and enable them to meet the highly demanding requirements for printed electronics. Another pretreatment of high value is web cleaning, since impurities that may settle on the substrate will affect the performance of the final product. Removing these particles will be key in providing a reliable product.

4.1.1.1 Plasma Treatment

Plasma treatment is a broad term used to describe a type of pretreatment which corona treatment falls under. Plasma fundamentally is a fourth state of matter in which a gas is submitted to a strong electromagnetic field or is heated. This decreases or increases the number of electrons, creating positive or negative charged particles called ions, and is accompanied by the dissociation of molecular bonds, if present. [354] The presence of a significant number of charge carriers makes plasma electrically conductive, so it responds strongly to electromagnetic fields. Researchers are attempting to use plasma treatments to control substrate surface properties and enable the ability to print structures smaller than the ink droplet size, which is approximately 55 micrometers in diameter. [355]

4.1.1.2 Corona Treatment

Plastic is a synthetic man-made material that consists of very long molecular chains. The ends of the chain are considered bonding points, but because the chains are so long, there are very few bonding points for inks. During corona discharge treatment, electrons are accelerated into the surface of the plastic causing the long chains to break apart, producing a multiplicity of open ends and bonding points. The ozone from the electrical discharge causes oxygenation, which forms new carbonyl groups on the surface, leading to a higher surface energy, as demonstrated in Figure 7. The result is an improvement of the chemical connection between the molecules in the plastic and the applied media/liquid. This surface treatment will not reduce or change the strength or the appearance of the material. The corona treatment only affects the molecular chains within 0.00001 micron of the surface. [356] Corona treatments typically do not have long life spans, so printing should take place immediately after the corona treatment for the best results.



Material – Basic	Dyne/cm
PP	29
PE-LD	31
PE-HD	32
BOPP	32

Process - Application	Dyne/cm
Print – solvent based ink	40-42
Print – water based ink	46-48
Coating	44-54
Lamination	46-56

Figure 7. Corona Treatments [357]

Manufacturing companies providing corona treatment equipment and support are as follows. The corona technology was developed in the UK by Verner Eisby in 1951. Today, there are two predominant companies in the UK: Vetaphone, the company that Eisby founded, and

Dynetechnology. There are several companies in the United States that produce their own manufacturing equipment to accomplish corona treatment. Enercon Industries Corporation (Wisconsin) and Tantec EST, Inc. (Illinois) are two U.S. companies that produce their own equipment. Tantec is a supplier to the electronics industry, and offers both plasma and corona treatment solutions, in addition to leak detection systems for non-conductive single layer materials.

Plasma treatments may be used in conjunction with corona treatments depending on the particular ink and substrate. Plasma and corona treatments are very similar, with just a few distinct differences. [358] Plasma treatment can enhance any surface and its effects last longer than corona treatment. However, corona treatment systems are cheaper, robust, user friendly, and easier to maintain. Many of the same companies that produce corona equipment also produce plasma equipment. As further applications are developed, industry standards may indicate which process is better or if both should be used for certain types of substrates and/or applications.

While there seems to be a significant amount of research occurring in Europe and Asia regarding pretreatments, there are several domestic universities researching the uses of pretreatments. Among them are Clemson University [359] and University of California Berkley. However, since both plasma and corona treatments are such widely used techniques across several different industries, companies and/or universities involved with plasma and corona treatments specifically for FHE applications could not be identified.

4.1.1.3 Web Cleaning

Web cleaning is an important treatment stage as a roll of substrate is unwound off the parent roll and before the ink is deposited on the substrate. As with any rolled materials, a certain amount of electrical charge (static) will build up on the surface as the roll is unwound, and that electrical charge will attract impurities to the substrate surface. Those impurities need to be removed to increase production yield and decrease imperfections. Teknek is a company out of the UK that has developed a roll cleaning system, Nanocleen, for flexible substrates. Nanocleen was developed as part of Clean4Yield, an EU-funded project coordinated by Holst Centre. [360] At this time, no U.S.-based company could be identified that had web cleaning technology equivalent to Teknek.

4.1.2 Application Methods

Similar to the many ways that materials can be deposited onto silicon to create ICs, various kinds of application methods are used to deposit materials onto both flexible and rigid substrates to create FHE. Some of the application methods used for FHE are exactly the same as the processes used to manufacture conventional electronics, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and electrochemical deposition (ECD). Other application methods are completely new to the electronics industry and are being investigated for use in FHE manufacturing, such as traditional graphics printing processes and industrial coating techniques. In this section, the various application methods that can be used to manufacture FHE, including deposition, printing, and coating, will be described.

4.1.2.1 Printing Methods

In order to fully appreciate the new developments in printed electronics, an understanding of conventional printing processes is fundamental. These conventional printing processes include lithography, offset lithography, photolithography, digital lithography, gravure, flexography, screen printing, thermal transfer printing, inkjet, and Optomec aerosol jet printing. The following sections will describe each of these technologies and demonstrate how they are being used in the FHE industry. Additionally, recent advances in FHE printing technology will be discussed, including various universities and companies developing innovative printing techniques specifically for FHE applications. For a quick summary of the some of the information contained in the following sections, please refer to Table 15 and Table 16.

4.1.2.1.1 Lithography

One of the oldest methods for printing is lithography, which dates back to 1796 [361]. This printing process was originally based on the premise that oil and water do not mix. An image was drawn with oil on a smooth lithographic limestone plate. The stone was treated with acid, which etched the portions of the stone not protected by the oil. When the stone was then moistened, the etched areas retained water, and an oil-based ink could be applied to only the image because it repelled the water in the etched areas. This ink was then transferred to a substrate to create a printed image. Today, lithography has been replaced to a large extent with offset lithography, but traditional lithography can still be found in some fine art printmaking applications. Most modern forms of printing are based on lithography fundamentals.

4.1.2.1.2 Offset Lithography

Offset lithographic printing on to a web (reel/roll) of paper is commonly used for high speed printing of newspapers and magazines. Often called offset printing, offset lithography was developed in 1875, and is also based on the basic idea of the repulsion of oil and water [362]. This method involves an image carrier that contains the image to be printed. The part of the image carrier with the image attracts ink from ink rollers, while the non-printing area attracts a water-based film, called fountain solution. The fountain solution keeps the non-printing areas ink-free while the image is printed onto a substrate. Fountain solution primarily consists of water with isopropyl alcohol and other additives to lower surface tension and control pH. [363] However, due to volatile organic compound (VOC) emissions, there is research being conducted to replace alcohol with glycol ethers to control surface tension. Figure 8 depicts a typical offset lithography setup.

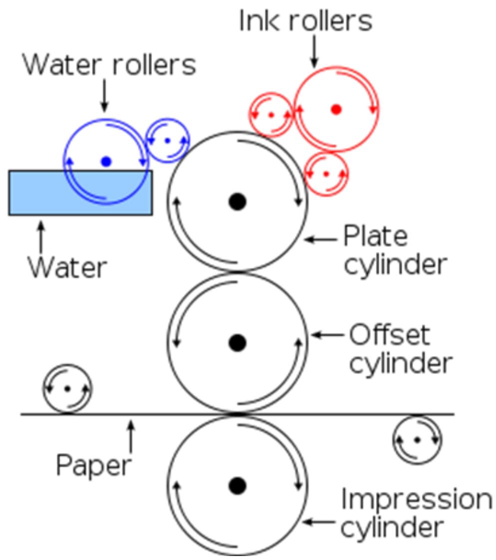


Figure 8. Offset Lithography [364]

There are four common types of lithographic inks: petroleum-based, vegetable oil-based, ultraviolet (UV) & electron beam (EB) curable, and heatset. [365] Lithographic inks are extremely viscous, almost paste-like, and are typically strong in color in order to compensate for the smaller amounts that are typically applied. Some of these thick paste-like inks, such as the petroleum and vegetable oil-based ones, contain solvents or drying oils to accelerate drying, which unfortunately leads to VOC emissions when they evaporate. Typically these drying oils are canola oil, but lately soybean oil has been used more frequently in order to reduce some VOC emission. UV & EB curable inks are desirable because of their low VOC content, but since these inks are still in the development stage, both the equipment and the inks themselves can be costly. [366] Heatset lithographic inks are desirable because of their quick drying feature, but the large solvent content that allows this characteristic also leads to significant VOC emission. Therefore, most presses that use heatset inks also are equipped with pollution control equipment.

Offset lithography offers a consistently high image quality. Other advantages include rapid and easy production of printing plates, which also tend to have a longer life than other types of printing plates. Lithography is a cost effective way of developing a high quality print in commercial printing quantities. [362]

There are disadvantages to offset printing as well. Although the image is high quality, the image is slightly inferior in quality to rotogravure or photogravure printing. Printing plates need to be cared for correctly or they can become sensitive (due to chemical oxidation) and lead to print in non-image areas. It is not cost effective to use offset lithography with small printing jobs due to the cost of producing the plates and setting up the printing press.

As previously mentioned, offset lithography deposits a relatively small amount of ink. However, in printed electronics, thin inks can make electrical conductivity difficult, and the use of an aqueous (water-based) fountain solution is often not good for polymers. Offset lithography is very similar to flexo and gravure in its printing of thin films for FHE, with only slight differences in the application of inks and imprint surfaces. Yet, because research and development (R&D)

today for offset is mainly focused on graphics or commercial printing, it is not expected to see significant innovations emerging for this technology for FHE—although it is clearly possible.

The most promising applications for offset lithography involve flexible organic displays, logic/memory, and photovoltaic (PV) layers where single, thin-film deposition is needed without excessive curing or sintering. [367]

A few literature examples can be found where offset lithography is used for FHE applications, and all of these examples are from the same group of researchers out of Brunel University in the United Kingdom. In 1999, this group presented at the First International Conference on Environmentally Conscious Design and Inverse Manufacturing. [368] Here they discussed the use of offset lithography to print passive electronic components and circuit interconnects.

Specifically, they deposited layers of metal and ceramic-loaded inks with offset lithography to create multilayer ceramic capacitor elements on flexible substrates. The same authors also published a paper in Electronics Letters in 1999 describing the production of RF circulator structures using offset lithography to print the conductive patterns on a wide range of flexible substrates. [369] In 2002, they published their work to create capacitive-type humidity sensors using offset lithography. [370] In 2007, this group moved on to voltaic cells [371], and in 2012, they created low cost, flexible electroluminescent displays with novel electrodes, both through the use of offset lithography. [372] No domestic university could be identified that was researching offset lithography methods for FHE.

Novalia, a start-up company founded by Dr. Kate Stone and based in Cambridge, UK, uses conductive ink and offset lithography techniques to create FHE products for the media, advertising, music, and healthcare sectors. [373] Novalia focuses on applications that create innovative and exciting ways to connect brands to their target audience. For example, they have created interactive posters and tissue boxes, paper keyboards, and smart sensors and speakers. In addition to offset lithography, Novalia also utilizes screen printing and flexography techniques. By using inexpensive printing techniques, Novalia hopes in the future that their innovations will enable people in developing countries to have access to modern technology for the first time.

4.1.2.1.3 Photolithography

The process of photolithography was developed in 1826 and was significantly improved through 1954. The process involves multiple steps of cleaning, preparation, photoresist application, exposure and developing, etching and finally photoresist removal. It is the standard by which most integrated circuits (ICs) and microprocessors are produced today. The cleaning method has various steps and the widely accepted standard for cleaning is called the Radio Corporation of America (RCA) method, which involves removal of organic contaminants, thin oxide layers, and ionic contamination, in that order. [374] The preparation phase involves heating of the silicon and additional chemical application to increase adhesion. [375] A spin coating technique is then used to apply the photoresist in a uniform thickness. Heat is applied to burn off any excess solvent from the photoresist. This step, often called soft bake, stabilizes the resist film. [376] The next step is exposure, where a mask is applied and the photoresist is exposed to UV light. There are various ways to complete the exposure step, but typically a mask is applied so only parts of the substrate are exposed to the light. The photo resist is then developed using an

aqueous solution. A baking process usually takes place after the developing to harden the final resist image. Next the pattern is transferred into the substrate usually by an etching method, but selective deposition or ion doping can also be used. Once the pattern is transferred to the substrate, the remaining photo resist is removed.

There are many disadvantages to photolithography including, but not limited to, the use of chemicals that are harsh for the environment and the humans working with them. As electronics become smaller, more production can occur in a given production batch. However this process is limited to only batch production and cannot be performed in a roll-to-roll setting.

Photolithography is the industry standard as of today, and on-going research to improve methods in photolithography are occurring.

Photolithography has remained a viable production method even though many in the industry thought it would go by the way side as electronics became smaller and smaller. For instance, by the early 1980s, many in the electronics industry had come to believe that features smaller than one micrometer could not be printed optically. Modern photolithography techniques using excimer laser lithography already print features with dimensions a fraction of the wavelength of light used – an amazing optical feat. New methods such as immersion lithography, dual-tone resist and multiple patterning continue to improve the resolution of 193 nm lithography.

Meanwhile, current research is exploring alternatives to conventional UV, such as EB lithography, X-ray lithography, extreme UV lithography, ion projection lithography and nanolithography. [377]

4.1.2.1.4 Digital Lithography

Digital lithography, performed at Palo Alto Research Center in California, is the process of jet printing an etch mask, and it is essentially a digital form of the photolithographic methods used in microfabrication. [378] Typically called maskless lithography, the process involves radiation being focused into a narrow beam and used to directly write an image into photoresist. [379] This process begins in a very similar fashion to traditional photolithography – a thin film of photoresist is deposited on a substrate through any means deemed necessary. Then, instead of using a photomask to protect some areas and expose others to the UV radiation, a narrow beam of radiation is used to target specific areas of the photoresist. After this step, the process continues just as in photolithography, where the desired areas of photoresist are removed to expose and etch the underlying layer, followed by removal of the remaining photoresist. This process can be repeated as many times as necessary until the product is completed.

4.1.2.1.5 Gravure

Around the same time that offset lithography was being developed, a printing method called gravure was gaining attention. Gravure printing is a very basic type of transfer printing where the desired image is etched directly on to a roll. The roll travels through an ink well and any excess ink is removed by a blade, commonly known as a doctor blade. The roll then travels up to meet the substrate where the ink is deposited with the help of an impression roll, as depicted in Figure 9. Typically the substrate then moves through a dryer section to set the ink. After the drying section, the substrate is ready to travel through subsequent printing stations if applicable.

The doctor blade is a very critical part of this printing process as this is where any excess ink is wiped from the print cylinder before it is deposited on the print surface. This places a stringent requirement on the quality of the roll, including surface roughness, hardness, and shape uniformity. It also places hard requirements on the quality of the doctor blade, and the pressure it applies to the surface. [380] Gravure rolls are typically made from a hard material, such as chrome coated copper.

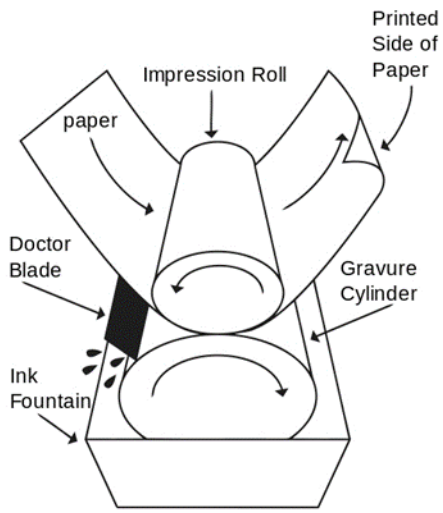


Figure 9. Gravure Roll-to-Roll Printing [381]

Gravure printing is advantageous for its ability to produce a high resolution print, which is highly desired when printing electronics. One major disadvantage of gravure printing is the cost involved in producing the printing roll. Due to the high cost of engraving the roll, it is only economically feasible to use this printing method for large scale production, similar to offset lithography. Gravure inks have a very low viscosity that allows them to be drawn into the engraved cells in the cylinder and transferred onto the substrate. [382] These inks can be both solvent and water-based which offer a handful of tradeoffs similar to inks used in offset lithography. The water-based inks require more energy to drive off the undesired components, but they are more environmentally friendly. Gravure printing methods have seen success using various inks, and specifically inks containing single walled carbon nanotubes (SWCNTs) to create thin film transistors (TFTs).

In the academic world, gravure printing is a widely used and researched technique for printing FHE. In fact, there are several examples of gravure being used to simply deposit conductive lines. In 2005, researchers from the University of Oulu in Finland used gravure to deposit conductive material onto paper and plastic films. [383] They were able to achieve a printed resistance of approximately 50 mΩ/sq with conductor lines that were 4 – 7 µm thick. These specifications were ultimately dictated by the substrate smoothness, not the printing method. Similar results were demonstrated by researchers from University of California at Berkeley in 2010 [384] and from Western Michigan University and Corning, Inc., in 2011. [385]

Gravure printing is often used to create electrodes for FHE applications. In 2007, researchers from Germany published an article describing their use of a direct gravure process to coat indium

tin oxide (ITO) nanoparticle patterns on polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) films to create transparent electrodes. [386] In 2012, researchers from Western Michigan University also used gravure printing to create transparent electrodes from ITO. [387] Similarly, in 2010, researchers from Sunchon National University (Korea), Paru Corporation (Korea), and University of California at Berkeley studied gravure printed electrodes in an effort to improve the surface roughness, thickness, line widening, and line-edge roughness of such devices for future printed electronics applications. [388] A team from Korea Institute of Machinery and Materials also published their efforts in 2010 describing their use of gravure printing to produce electrodes for flat panel display devices. [389] Researchers from Dai Nippon Printing Co., in Japan have also used gravure technology to create OLED posters for applications such as electronic books and electronic paper. [390]

Gravure printing has also been used to create other FHE devices, including transistors, sensors, and antennas. In 2010, researchers from Chemnitz University of Technology in Germany created fully printed organic field effect transistors (OFETs) using gravure technology. [391] Two years later, researchers from University of California at Berkeley and Sunchon National University in Korea developed a micro-gravure printing process to create high-performance printed TFTs with excellent DC and AC characteristics. [392] A team from Western Michigan University used gravure printing to create electrochemical biosensors by printing a silver nanoparticle-based ink onto a PET substrate. [393] The gravure printed biosensors were able to detect chemicals at levels as low as picomolar. Finally, in 2012, roll-to-roll gravure technology was used to successfully print rectennas (antenna, diode, and capacitor) onto plastic foils for wireless power transmission. [394]

In addition to being used for several different applications within the academic world, gravure printing for FHE is also very popular in the commercial world. The IDTechEx report from December 2014 on Printing Equipment for Printed Electronics 2015 – 2025 highlights several companies involved in gravure printing, including Bobst, W.R. Chestnut Engineering, Inc., Komori Corporation, Nilpeter A/S, Yasui Seiki Co., Harper Corporation of America, and Ohio Gravure Technologies, Inc., which range from graphene equipment suppliers to graphene roll engravers. [395]

Bobst, W.R. Chestnut Engineering, Inc., Komori Corporation, and Nilpeter A/S all manufacture and provide gravure printing presses. Bobst, headquartered in Switzerland with a North American location in New Jersey, offers coating & laminating, printing, and converting products. [396] Their gravure equipment fall within their printing product line, and they offer systems targeted for high speed, low waste, niche markets, paperboard packaging applications, solar panels, and decorative printing, among others. W. R. Chestnut Engineering, founded in 1973 and located in New Jersey, offer narrow web press equipment, including high quality, short run rotogravure printing equipment; low-cost, compact narrow web flexo/gravure presses; systems capable of performing screen printing, flexo, and gravure in any combination; medium to long run rotogravure presses; and offline converting & finishing systems. [397] Their equipment has also allowed many companies to innovate new products, one of which was antennas for security/radio frequency identification (RFID) labels. Komori Corporation, headquartered in Japan with an American location in Illinois, has been a leader in manufacturing printing equipment since 1923. [398] Their products include short run offset systems, curing systems,

high performance offset printing equipment, high speed printing systems, and roll-to-roll gravure and offset systems with incorporated post-processing capabilities. Some of their systems even offer an automatic ink roller cleaning function. Nilpeter, headquartered in Denmark with a technology center in Cincinnati, Ohio, was established as a local press manufacturer in 1919. [399] Today they offer flexo and offset presses, with additional converting, embossing, gravure, and screen units. Their systems are targeted for food & beverage, health & beauty, multi-web, phone card, sleeve label, stamp, tube laminate printing, and wine & spirits applications. While none of these four companies explicitly state on their website that their equipment can be used for printed electronics applications, it can be assumed that their technology would be easily transferrable to the FHE industry.

Yasui Seiki Co., headquartered in Japan with U.S. operations located in Indiana (U.S. location called Mirwec Film, Inc.), has developed a Microgravure™ coating method in response to the need for a smooth and uniform thin layer coating technique offering simplicity, reliability, and reproducibility. [400, 401] This system has gravure roll diameters between 20 – 50 mm, whereas traditional gravure roll diameters range from 125 – 250 mm. The smaller diameter leads to a smaller contact area, which allows for better quality printing. The Microgravure™ system is designed to work with several different substrates, including PET, foils, paper, glass felts, cloth, Kapton, polypropylene (PP), polyethylene (PE), and other specialty films, and can has been used in electronics, graphics, medical, optical, battery, industrial, and automotive applications.

Microgravure™ applications specifically related to FHE include photoresist layers, transparent conductive layers, insulating layers, various layers for LCD and OLED displays, anti-static layers, conductive polymer layers, skin contact electrodes, anti-reflective coatings, paper batteries, and chemical treatment coatings for film substrates.

In addition to companies that produce entire gravure printing systems, the IDTechEx Printed Electronics Equipment report mentioned above [395] also included companies that are involved specifically with the gravure rolls used in the gravure printing processes. One of these companies is Harper Corporation of America, which was founded in 1971 and is currently headquartered in Charlotte, North Carolina. Harper produces anilox rolls for flexo printing, coating rolls, and gravure cylinders. [402] Harper's rolls and cylinders are designed for rigorous coating and laminating processes, including the application of UV, solvent-based, and water-based inks, metallic inks, fluorescent and iridescent inks, and other specialty coatings. Ohio Gravure Technologies, Inc., located near Dayton, Ohio, is a precision equipment design and software development company that has a broad and deep expertise in gravure printing. [403] Specifically, they design, build, and support gravure roll engraving machines and the accompanying software for these machines. Lately, their experience has allowed them to expand beyond the printing into the printed electronics and optical industries.

4.1.2.1.6 Flexography

Flexography can be easily thought of as a modern day letterpress. Flexography, developed around 1890, is similar in function to gravure, but differs in the way that the master images or image carriers are created. [404] In this method, an image negative is placed over a plate made of light sensitive polymer. The plate is then exposed to UV light, curing the portions of the plate

exposed to the light and leaving the other portions uncured. The plate is washed in water or solvent and the uncured portions are washed away, resulting in a plate with the image on it. Other methods of making these plates include laser etching and metal molds. These image plates are then placed into slots on the plate roller. An ink roller is partially immersed in an ink bath, and as it rotates, it transfers ink to the plate roller. The coated plate roller then rotates and transfers the image to the desired substrate. Flexography can be utilized on a wide range of substrates including plastic, metallic films, cellophane, and paper. It is used in the food, beverage and healthcare industries and is often used to print large areas of solid color.

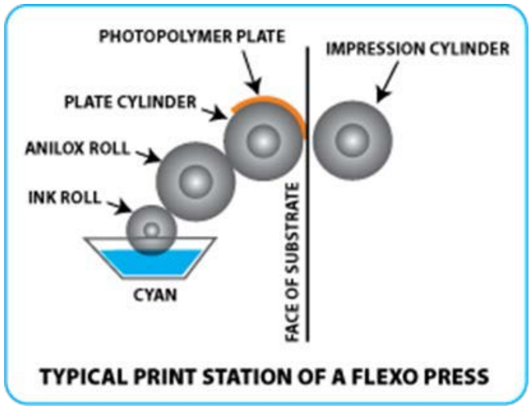


Figure 10. Typical Flexography Print Station [405]

There are many advantages to flexography. The production is very high volume, and the master plates are easily made and inexpensive to produce. Flexographic inks are fast drying and have a low viscosity. [406] They are formulated to be non-penetrating and simply sit on the surface of nonabsorbent substrates until solvents are removed and they solidify. The printing process is conformal and tolerant of substrate abnormalities such as deformation, which is desirable if the substrate begins to slightly deform due to the temperature of the inks. [367]

Unfortunately, flexography has limited resolution capability. Additionally, some combinations of plate material and solvents may cause the printing plate material to swell or change its viscoelastic properties, but work is ongoing by leaders in the flexography plates to develop a solution for printed electronics technology. [407]

Flexography is ideal for printed electronics applications that require a single ink to be applied to a heat sensitive substrate. Flexographic printing is also starting to gain acceptance with transparent conductor grids and other nano-particle-dispersion conductor applications [367].

Several examples can be found in literature of flexography being used for electronics applications within the academic world. For example, in 2004, researchers from the Rochester Institute of Technology published an article describing their work to create RFID tag antennas. [408] For this experiment, both rotary letterpress and flexographic printing were investigated to create electrically conductive structures through printing of a silver flake ink dispersion. A variety of flexographic printing parameters were evaluated as a part of this study, including inking time, inking speed, printing speed, and printing force.

In 2011, a team from Singapore Institute of Manufacturing Technology presented their work using flexography for electronics at the 13th IEEE Electronics Packaging Technology Conference. [409] They discussed their use of flexography and solvent-based conductive ink to create conductive grids that had a sheet resistance that was approximately 50 percent lower than ITO film. Researchers from VTT Technical Research Centre of Finland and Aalto University in Finland presented their work at the 2014 Electronics System-Integration Conference. [1] They demonstrated a low-cost, high volume manufacturing process to produce an electronic anti-tampering indicator on a paper substrate. Their demonstrated manufacturing process utilized flexo printing to apply conductive and adhesive layers to the electronic structure. Additionally, researchers from Loughborough University in the United Kingdom recently published work in March 2015 regarding electrodes created through flexographic and offset lithography printing techniques. [411] These electrodes were then used to create printed rechargeable power sources. The electrodes printed with flexography resulted in a desirably higher capacitance as compared with the ones printed with offset lithography.

Since flexography is one of the forerunners as a printed electronics manufacturing method, along with gravure and screen printing [407], many companies are invested in flexography equipment and technology, just as many researchers are using flexography as a R&D technique, as demonstrated above. Many of the companies mentioned in Section 4.1.2.1.5 for gravure printing, including Nilpeter A/S and Harper Corporation of America, also have flexography capabilities as well. Nilpeter A/S offers a large line of flexography systems that are designed for multi-substrate printing, high performance, and durability. As mentioned above, Harper Corporation of America produces anilox rollers for flexographic printers that can tolerate rigorous coating and laminating processes and are even compatible with metallic ink formulations.

Other companies focus more heavily on flexography equipment, including The Gallus Group, Mark Andy, Multi Print Systems (MPS), and OMET, but none of them feature machines specifically targeted for FHE applications. The Gallus Group, which has North American headquarters in Pennsylvania, manufactures flexo presses designed specifically for the label industry that are compatible with a variety of substrates, including paper, plastic, and foil. [412] Their systems offer various features, including affordability, multi-substrate capabilities, minimal waste, high productivity, quick reconfigurability, and high performance. Mark Andy, located in Missouri, has been involved in the label and packaging industry for over 65 years through the design and manufacture flexography printing machines. [413] Similar to The Gallus Group, Mark Andy's various systems offer fast set-up and changeover, shorter web paths, low waste production, high quality, and consistent and accurate prints. MPS, headquartered in The Netherlands, has produced flexo printing presses since 1996. [414] Their North American organization, located in Wisconsin, offer local press assembly, sales, service, and support. MPS flexo systems range from cost-efficient to highly-advanced, fully automated machinery that serve all segments of the self-adhesive label, flexible packaging, printing, and converting industries. OMET, an Italian company, offers a line of flexo printing machines that guarantee high quality and significant waste reduction. [415] OMET's systems are intended for self-adhesive labels, unsupported filmic labels, shrinkable films, aluminum packaging, paper labels and packaging, and folding cartons. However, they are also the only flexo equipment company found that identifies specialty applications for their equipment, which includes RFID labels, smart labels,

parking and transit tickets with magnetic bands, anti-counterfeiting materials, and security materials.

4.1.2.1.7 Screen Printing

Screen printing was developed around 1910 and involves using a stencil to create the desired image. [416] A stencil of the image is prepared and placed underneath a mesh screen. Ink is then pulled across the screen with a sharp-edged squeegee. The ink is pushed through the mesh and either stopped by the stencil or pushed all the way through to the substrate underneath the stencil to create the image, as shown in Figure 11.

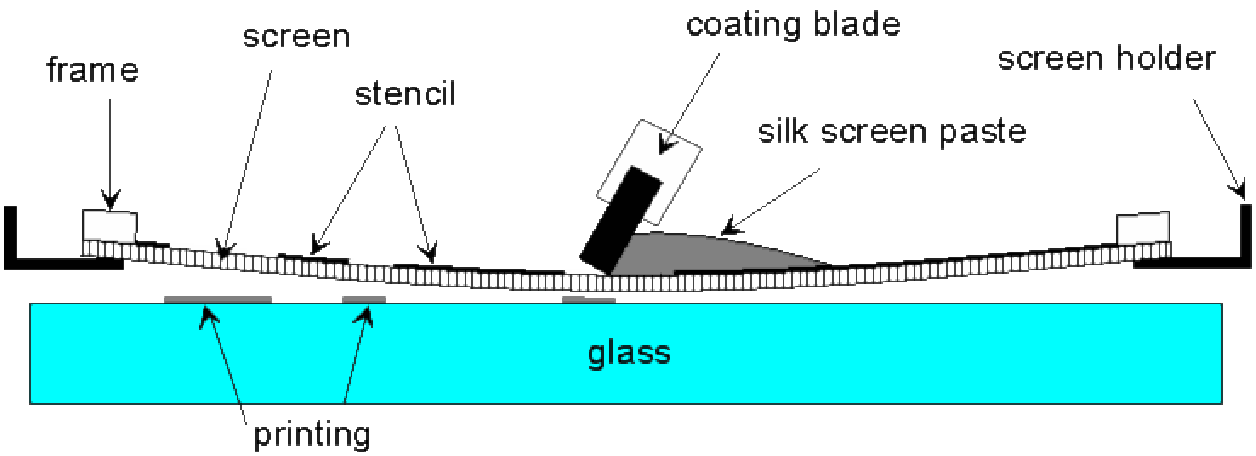


Figure 11. Screen Printing Process [417]

One benefit of screen printing is that a thicker layer of ink can be applied, which opens the door for interesting effects not possible with other methods. [418] Also, because of the simplicity of the process, a wide range of inks are available for use. Screen printing inks are moderately viscous and have a paint-like consistency. Screen printing inks have similar composition to other printing inks (pigments, solvents, additives) and fall into five categories: solvent, water, solvent plastisol, water plastisol, and UV curable. The solvent and water-based screen printing inks are very similar to the solvent and water-based inks from other printing methods like flexography and offset lithography. Plastisol inks, thermoplastic polyvinylchloride (PVC)-based systems that contain very little solvent, are used predominately in the textile screen printing industry. UV curable inks are comprised of liquid prepolymers, monomers, and initiators that crosslink to form a dry thermosetting resin when exposed to UV radiation. [419] They require less energy to dry than solvent or water-based inks, but they are more expensive and have more safety issues.

In general, the advantages and disadvantages of screen printing are similar to those of offset lithography, but screen printing is preferred for printed electronic applications that require thick layers of material to achieve high levels of electrical conductivity or resistance [367].

Screen printing is widely accepted across the industry as the most established technology for the production of printed electronics technology. [367] For FHE, screen printing techniques are most widely used in the production of printed circuit boards (PCBs). Specifically, it is useful for FHE applications that require thick layers of materials, such as OLED/EL displays, batteries, PV technology, membrane switches and touch panels, sensors, and glucose test strips. The thick

layers of applied material that is characteristic of screen printing help to achieve high levels of conductivity or resistance.

4.1.2.1.8 Thermal Transfer Printing

Thermal transfer printing, depicted in Figure 12, has not received much attention in the printed electronics industry in the past, but it has some advantages that might make it a suitable option in the future. [420] The printing process begins with the production of a thermal transfer ribbon that is constructed out of polyester film. On one side of the film, a heat resistant slip layer is coated, and on the other side the ink material/design is coated. The ribbon construction can be simple and single layered, or it can be complex and involve a multi-layer design featuring layers with various functionalities. The ribbon is then conveyed under a thermal printhead, which transfers the ink using heat and pressure to the desired substrate. Today, one of the leaders in thermal transfer ribbon technology is Iimak, located in New York.

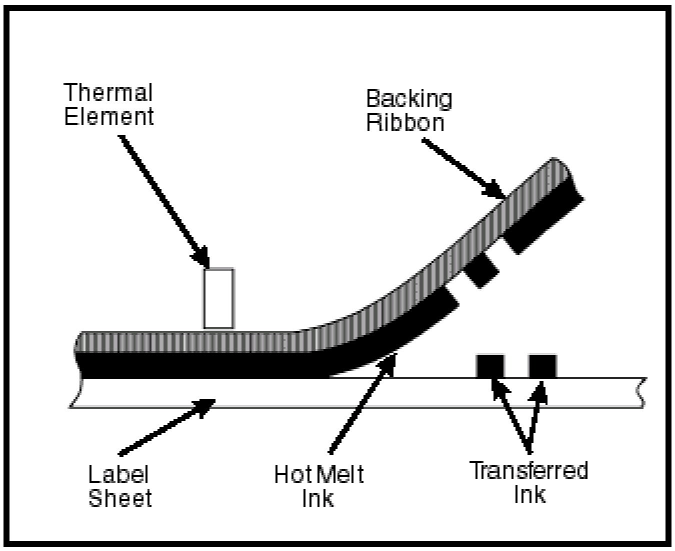


Figure 12. Thermal Transfer Printing Technique [421]

As aforementioned, thermal transfer printing is not yet a leading technology for the FHE industry, but some universities have investigated its potential for electronics manufacturing. In 2003, John Rogers from Bell Laboratories (now at University of Illinois Urbana-Champaign) published a report documenting research performed in collaboration with DuPont Central Research on the use of microcontact printing and thermal transfer printing as patterning techniques for plastic electronics. [422] Through their research, they determined that there is significant flexibility in the type of materials that can be patterned using thermal transfer printing. It is also a completely dry and additive process, eliminating the need for etchants and solvents. However, thermal transfer printing does not offer extremely high resolution, and adhesion between the various layers needs to be closely monitored throughout the process.

4.1.2.1.9 Inkjet

One of the newer innovations in printing technology is inkjet, which was developed in 1951. [423] Inkjet creates a digital image by propelling droplets of ink onto a substrate. There are two different types of inkjet printing: continuous inkjet (CIJ) and drop-on-demand inkjet (DOD), as

shown in Figure 13. The CIJ process creates a stream of ink droplets that are directed to certain places by way of an electrostatic field that puts a variable electrostatic charge on each droplet. The stronger the charge, the further the droplet travels. Charged droplets are separated by one or more uncharged droplets to minimize electrostatic repulsion between droplets. The uncharged droplets are collected and recycled throughout the process. The DOD inkjet process on the other hand only applies a droplet when it is needed, using a thermal or piezoelectric mechanism. In the thermal mechanism, a pulse of current triggers a heating element to vaporize some of the ink in the nozzle chamber. This vaporization causes a bubble to form, leading to a pressure increase that propels a droplet of ink through the nozzle and onto the substrate. The piezoelectric mechanism involves a piezoelectric material within the chamber. When a voltage is applied, the piezoelectric material changes shape, again leading to a pressure increase that propels a droplet of ink through the nozzle and onto the substrate.

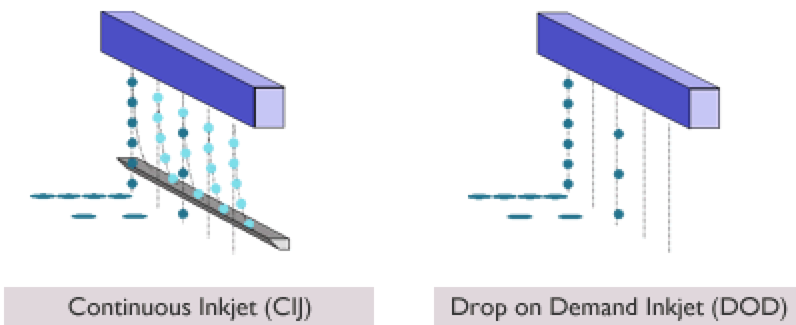


Figure 13. CIJ vs DOD Inkjet Technology [354]

Four main types of inkjet inks exist today: phase-change, solvent-based, water-based, and UV curable. [425] Other types, such as oil-based and liquid toner, exist but are much less common. Phase-change inks are hot melts that are distributed in solid form, melt before being printed, and then solidify quickly after application. Their fast drying nature does not allow them to spread, making them easy to control, but lacking durability and abrasion resistance. Solvent-based, water-based, and UV-curable inkjet inks are all very similar to other corresponding inks discussed previously, with regards to both their compositions and trade-offs.

Inkjet printing is widely recognized as a key enabling technology for printed electronics, and therefore, a very large portion of the various industrial, academic, and government organizations involved in the printed electronics industry utilize inkjet technology. [426] Inkjet printing systems are typically inexpensive, have a relatively small footprint, deposit a wide range of materials onto a large variety of substrates, require relatively small amounts of ink sample, have minimal material waste, can fabricate devices directly from computer aided design (CAD)/computer aided manufacturing (CAM) files, and are easily adaptable. [426-429] All of these features have made inkjet printing ideal for R&D environments, but it is also compatible with large-scale industrial production for many of the same reasons. Other benefits of inkjet printing, specifically for flexible electronics, are its non-contact and additive natures, which eliminate contamination and defects and allow for ink to be placed precisely where desired. Inkjet printing systems have successfully achieved resolutions as small as 10 – 20 µm, which is approximately five times better than screen printing.

So far, inkjet printing technology has been demonstrated for electrical and optical interconnects, various types of displays, sensors, medical diagnostics, drug delivery, MEMS packaging, photovoltaics, three dimensional (3D) rapid prototyping, electrodes, field effect transistors, ICs, conductive polymer devices, RFID tags, batteries, and printed circuit boards.[426-429] In the future, inkjet will most likely continue to be used heavily for FHE applications, particularly within R&D environments, where low-cost and high adaptability are valuable.

4.1.2.1.10 Optomec Aerosol Jet Technology

Aerosol Jet technology, developed by Optomec is a printing method that utilizes aerodynamic focusing to deposit inks and other materials. [430] The process, depicted in Figure 14, begins by atomizing a material (ink) with an atomizer (either ultrasonic or pneumatic), which is then condensed into a concentrated aerosol mist. The mist, which is surrounded by a focusing gas, is directed to a nozzle head to deposit the material onto the substrate. Because the droplets are always surrounded by the focusing gas, they never have a chance to touch the walls of the nozzle and cause clogging. [431] This means that the deposition materials can be much smaller than the size of the nozzle orifice, allowing the use of nanomaterials. After deposition, the materials can then be thermally or chemically processed to obtain their final properties. [430]

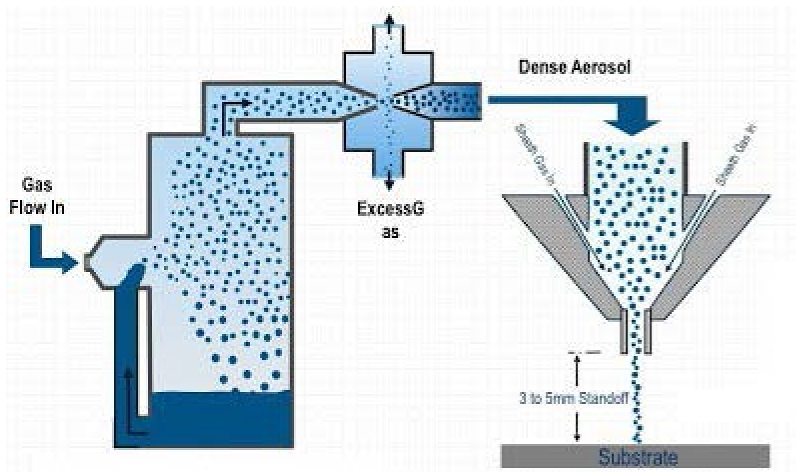


Figure 14. Optomec Aerosol Jet Printing Technology [355]

Aerosol Jet Printing was developed as a way to direct-write high viscosity fluids in a non-contact process. [431] The wide range of viscosities this system is capable of handling is made possible through the use of various atomizers. For lower viscosity materials, an ultrasonic atomizer nebulizes the fluid with high-frequency pressure waves. For high viscosity materials, a pneumatic atomizer uses a high velocity gas stream to shear the liquid into droplets.

The Aerosol Jet process was originally designed to fill a gap in the microelectronics fabrication environment. [433] Up until the point that Aerosol Jet Printing was invented, current manufacturing techniques of the time could create very small electronic features, through methods like vapor deposition, and very large features through techniques like screen printing. No technology was capable of adequately reaching the micron (10 – 100 µm) level, and therefore, Aerosol Jet Printing was created to address that gap. Today, Aerosol Jet has been used to successfully demonstrate many more advanced applications including, high-efficiency solar cells; high-efficiency fuel cells; EMI shielding; fully-printed thin-film transistors; embedded

resistors, antennae, sensors, etc.; flexible displays; flexible circuitry; and high-density assays for drug discovery.

In the last five years or so, several different academic institutions have investigated the Aerosol Jet Printing process for use in flexible electronics applications. For example, in August 2010, researchers from University of Minnesota and Northwestern University used Aerosol Jet technology to print aqueous CNT inks on plastic to form digital circuits. [356] In 2012, a team from the Chinese Academy of Sciences used Optomec's systems to fabricate CNT TFTs on flexible substrates. [435] A team from Oak Ridge National Laboratory presented at the 2012 Future of Instrumentation International Workshop and described their efforts to use Aerosol Jet technology to integrate additive manufacturing and printed electronics to create flexible 3D microscale electronics structures. [436] In 2013, researchers from University of Minnesota and Yeungnam University in Korea used Aerosol Jet Printing to fabricate an electrolyte-gated transistor based on polymeric semiconductor materials. [437]

For the time being, Optomec appears to be the only company with this type of printing capability, and they hold many granted and pending patents for their proprietary process and equipment. As demonstrated above, several organizations and research institutions are investing in Aerosol Jet technology for printed electronics development. Therefore, it can be expected that Optomec's Aerosol Jet Printing technology will continue to be a popular printing tool for both R&D and industrial environments in the FHE industry, especially because of its capability of handling several different material types.

4.1.2.1.11 Comparison of Printing Methods

Table 15 offers a comparison and summary of the various printing methods used for FHE that are described in the proceeding sections. This includes information about resolution capability, printing inks, viscosity ranges, drying mechanisms, compatible substrate characteristics, etc.

Table 15. Printing Methods for FHE [429, 420, 438, 439]

Printing Method	Characteristics & Considerations
Offset Lithography	• Paste-like and tacky inks (viscosity = 30 – 100 Pa·s) • Non-volatile solvents and oils typically used to cause a long inking path • Elastomeric inking rollers eliminate use of strong solvents that could cause roller softening and/or swelling, which leads to a limited list of binder chemistries that are soluble in weak solvents • Undesirable emulsification of fountain solution into the ink • Drying by absorption, oxidation, chemical drying, or radiation • Can achieve resolutions of approximately 25 microns
Gravure	• Low viscosity inks (0.02 – 0.2 Pa·s) for acceptable flow performance • Highly volatile solvents allow for rapid release of solvent and quick transfer • Good lubricity, low abrasion, and low corrosivity to minimize wear on equipment (doctor blade and cylinder life) • Printed films dry mainly by evaporation with some absorption into the substrate • Can print down to 50 micron levels
Flexography	• Slightly wider processing range for viscosity than gravure (0.05 – 0.5 Pa·s) • Flexo plate not compatible with several solvents, limiting solvent selection for inks • Acceptable ink re-solubility and evaporation rate to avoid ink build-up on raised area edges of plate and decreased printed feature definition • Typically dried through evaporation, absorption, or radiation curing (aqueous and UV inks common for flexography) • Reaches approximately 30 micron feature sizes
Screen	• Intermediate viscosity (0.5 – 50 Pa·s) allows ink to flow through mesh and then level out to maintain structure and definition • Ink solvents should not swell or crack squeegee rubber or stencil film • Drying by evaporation, oxidation, or UV curing • Creates features of approximately 50 microns
Thermal Transfer	• Readily available thermal transfer printheads range in resolution from 400 – 600 dots per inch (dpi), but 1200 dpi and 2600 dpi are being developed. • Designed for printing mainly on flexible substrates • Can print very sharp, well defined lines • Substrates typically have a thermal coating to protect them from the heat used during application
Inkjet	• Very low viscosity (0.001 – 0.04 Pa·s) and preferably Newtonian fluid characteristics • Surface tension between 28 – 35 mN/cm for optimal droplet formation • Dispersion stability and small particle size, and use of less volatile solvents helps to prevent nozzle clogging • Use of mixtures of low and high boiling point solvents, in addition to controlling drying temperature, helps to eliminate coffee-ring effect • Drying by absorption, evaporation, or UV curing • Can pattern at resolutions of 10 microns
Aerosol Jet	• Maskless, low temperature nanomaterial additive process • Capable of patterning line widths and features between 10 µm – 1 cm • Acceptable material viscosity of 0.7 – 30 mPa·s (ultrasonic atomizer) and 1 – 2500 mPa·s (pneumatic atomizer)

4.1.2.1.12 Advantages and Disadvantages of Printing Methods

Table 16 provides a concise snapshot of the various advantages and disadvantages of the different printing methods that can be used to manufacturing flexible electronics.

Table 16. Advantages and Disadvantages of FHE Printing Methods

Printing Method	Advantages	Disadvantages
Offset Lithography [440]	• Printing plates are fast and easy to produce • Good for high-volume printing • Printing process itself is cost effective	• Printing quality not as good as gravure • Printing plates require maintenance and care • Expensive for small quantities
Gravure [441]	• Simple mechanical features • Excellent printing quality • High degree of consistency • Suitable for a number of substrates, including flexible • Good for long production	• High engraving costs • Not feasible for short runs
Flexography [441]	• Good process quality and line printing • Fast changeover and easy clean-up • Less expensive plate costs • Can print on various substrates	• Rolls have to be replaced more frequently due to wear • High drying costs • Less consistent printing quality than gravure
Screen [416]	• Can be used on several different substrates • Can print thick layers of materials • Ideal for R&D activities	• Longer set-up times • Only one color can be printed at a time
Thermal Transfer [420]	• Ability to print sharp and well defined lines • Controlled and uniform thickness of lines • Waste minimization • Designed for flexible substrates	• Not as applicable for rigid substrates • Substrates sometimes require thermal protective coatings
Inkjet [423]	• Low cost and easy to use • Can print fine and smooth details with good resolution • Reasonably fast with no warm up time necessary	• Printhead less durable and prone to clogging and damage • Replacement ink cartridges are expensive • Not appropriate for high volume printing
Aerosol Jet [430] [442] [431]	• Applicable for many different materials and substrates • Can support high volume production needs • Capable of depositing nanomaterials • Low temperature processing conditions • Appropriate for materials with a wide range of viscosities	• Droplet carrier gas creates cloud of powder in surrounding print area • Carrier gas causes localized crystallization at the pattern, leading to decreased bonding quality • Separate systems for the atomization and delivery of the fluid can lead to increased cost and complexity

4.1.2.1.13 Recent Advances in Printing Methods

Even though most of the previously described printing methods can be used to print electronics, many university and companies are researching and inventing new methods and applications to further move printed electronics a manufacturing technology.

Northeastern University's Center for High-rate Nanomanufacturing (CHN) has developed a fully automated nanoscale prototype printing system. [443] This Nanoscale Offset Printing System (NanoOPS) is based on directed assembly and transfer of nanoparticles. [444] To begin the process, a reusable damascene template is created out of either flexible or rigid materials.

Nanomaterials are then assembled onto the template in a particular pattern using electrophoresis. Finally, the assembled nanomaterials are transferred to a substrate to create the printed pattern. This new process, whose prototype was demonstrated in September 2014 [445], can print down to 25 nm levels and will theoretically cost and operate at a fraction of current nanofabrication technology. [443]

The Agile Technologies for High-performance Electromagnetic Novel Applications (ATHENA) group at Georgia Institute of Technology has been developing an innovative inkjet-printing platform that can print complex, vertical ICs directly from a desktop inkjet printer. [446] As part of this effort, inks were developed to work with a standard inkjet printer's piezoelectric nozzles. Researchers at Georgia Tech have created highly efficient electronic inks by employing the properties of nanoparticles of highly conductive materials such as copper, silver and gold. These nanoparticles are suspended in a solution, and then once delivered to the substrate via the nozzles are heated at a low temperature, which melts the conductive nanomaterials without deforming the substrate. By loading these nanomaterial-based conductive, dielectric, and sensing inks into the different-colored cartridges of a desktop inkjet printer, 3-D electronics topologies, such as metal-insulator-metal (MIM) capacitors, can then be created by printing the different inks on top of each other in a layer-by-layer deposition. Since printing is a non-contact additive deposition method, and the processing temperatures are below 100^0C, these inks can be printed onto virtually any substrate. These include standard photo paper, plastic, fabrics, and even silicon wafers to interface with standard ICs with printed feature sizes below 20 µm. This technology allows for rapid prototyping and experimentation, but can also be adapted to larger scale production.

Headquartered in Pittsburgh, PA, Advantech US has developed an Evaporation Printing vacuum deposition system for manufacturing microelectronic devices. This system uses additive manufacturing technology that performs in-line material deposition through shadow masks with precision alignment. [447] The company reports that the Evaporation Printing process has shown significant potential for the fabrication of chip packaging, microelectronic devices, circuitry, ePaper display backplanes and organic light emitting diode (OLED) display front panels, and is compatible with a number of both rigid and flexible substrates using bulk deposition materials. The key to their Evaporation Printing system is its additive process, which differs substantially from photolithography (today's standard for chip production). Advantech's shadow mask can produce feature sizes down to five microns, and they have used optics to reach a registration of one micron.

MesoScribe Technologies has developed a proprietary Direct Write Thermal SprayTM (DWTS) technology that enables the printing of harsh environment sensors and structurally integrated electronics. [448] The DWTSTM process allows for the printing of conductors, dielectrics, and polymer blends directly onto surfaces of components, whether it is flat or curved. This automated process is compatible with various printing area sizes, and can be used to deposit metallic or

ceramic coatings over a surface's entire area or only in specified locations, without masking or post-process patterning. This selective deposition is advantageous for antenna ground planes, electrical shielding, environmental barriers, and thermal management, and has been used to produce thermocouples, heat flux sensors, strain sensors, damage detection sensors, integrated wiring and conformal antennas. Figure 15 depicts MesoScribe's DWTS system.

Figure 15. MesoScribe Technologies Direct Write Thermal Spray™

4.1.2.2. Deposition Methods

Deposition techniques are one of the building blocks for conventional manufacturing of microelectronics devices. Deposition processes, including PVD, CVD, and ECD, are used to create thin films of material that are ultimately combined and built up to create electronics devices. Though not defined by a firm standard, these thin films typically range from a few nanometers to about 100 micrometers in thickness. [449] While some of these deposition processes are limited by their need to operate at extremely high temperatures, many of them can also be used to fabricate FHE. Compared to printing methods that are typically used to create patterns of conductive, dielectric, and/or semiconducting material, deposition methods for FHE applications are often used to create thin films of material on large areas that do not require significant patterning. While this is certainly not always the case, as will be seen with a few of the following deposition methods, it seems to be more of a general trend emerging with FHE manufacturing.

This section is comprised of analyses of several different deposition methods, including CVD, atomic layer deposition (ALD), PVD, sputtering, evaporation deposition, pulsed laser deposition (PLD), ion plating, electrospray deposition, epitaxy, and plating. Each analysis includes a general summary of the technology, followed by examples of the deposition technology being used in FHE applications. Additionally, various companies are provided for each technique that either perform the particular deposition method or produce deposition equipment.

Table 17 provides a snapshot summary of the information described in the following deposition sections. The categories across the top of the table are the main topics of interest when

discussing a particular deposition method. The color-coded boxes give insight into how each deposition method performs with respect to each category. A green box indicates that the deposition method performs well for that category, while a red box indicates that particular area is not a strong suit of the deposition method. Yellow boxes indicate that the deposition method does not excel nor lag behind in that particular area.

Table 17. Summary of Characteristics of Deposition Methods for FHE

	Coat Complex Geometries	Deposition Rate	Purity / Quality of Coating	Application Temperature	Control over Film Thickness / Composition	Cost	Roll-to-Roll Compatible
CVD	Green	Green	Green	Red	Green	Red	Red
ALD	Green	Red	Green	Yellow	Green	Red	Green
Sputtering	Yellow	Red	Red	Green	Red	Red	Green
Evaporation	Red	Green	Red	Red	Red	Green	Green
PLD	Red	Green	Red	Green	Green	Yellow	Green
Ion plating	Red	Red	Green	Red	Green	Red	Yellow
Electrospray	Yellow	Green	Green	Green	Green	Green	Green
Epitaxy	Yellow	Green	Green	Yellow	Red	Red	Yellow
Plating	Red	Red	Red	Yellow	Yellow	Green	Green

4.1.2.2.1. Chemical Vapor Deposition

CVD, in its most basic form, involves flowing precursor gas(es) into a chamber that contains heated objects to be coated. [450] The gases react on or near the hot surfaces, causing a thin film to be deposited onto the surface of the objects. The chemical by-products of the reaction, in addition to any unreacted precursor gas, is then removed from the chamber. A simple schematic of this process can be found in Figure 16. CVD has countless variations, and one of which, plasma-enhanced CVD (PECVD), is used for flexible electronics. PECVD allows materials to be deposited onto surfaces at lower temperatures than that of standard CVD. [451] In this process, the gases are introduced between two parallel electrodes which excites the gases into a plasma. A reaction takes place and the reactant is deposited onto the intended surface, which is typically between 250 – 350 °C, as compared to standard CVD where the substrate is at 600 – 800 °C.

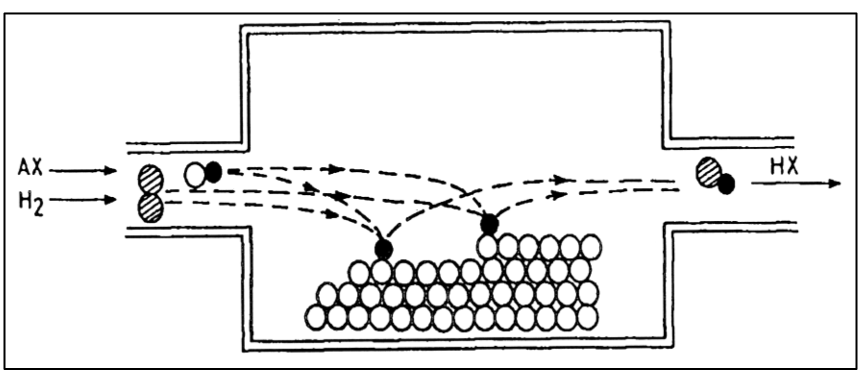


Figure 16. Basic CVD Process [452]

One characteristic that makes CVD stand out is its ability to deposit quite conformal coatings, including on the inside and undersides of object features. [450] CVD can deposit a wide variety of materials, at very high purity, and at relatively high deposition rates. Unfortunately, in order for a material to be applicable for this process, the precursor needs to be volatile near room temperature. CVD precursor materials also tend to be toxic, explosive, or corrosive, and the byproducts of the reactions that take place within the chamber can be hazardous as well. Despite all of this, probably the most widely recognized disadvantage of CVD is its requirement of operating at high temperatures, which eliminates several substrate options. The high temperatures also lead to stresses in the deposited films because of the difference in thermal expansion coefficients between the films and the substrates. However, the different variations of CVD, including PECVD, help to address some of these innate disadvantages.

CVD has been a critical enabling technology in conventional silicon-based microelectronics, and today it is used to deposit thin films of active semiconductor material, conductive interconnects, and insulating dielectrics. [450] CVD is also being investigated for use in FHE, specifically with applications involving graphene. In 2010, researchers from University of Southern California proved that continuous, highly flexible, transparent graphene films could be deposited through CVD for applications in PVs. [453] The graphene films, which were being grown using CVD and then transferred to transparent substrates, were being used as transparent conductive electrodes in organic photovoltaic (OPV) cells. The researchers believe the continuous nature of the CVD process, which led to minimal surface roughness of the graphene films, contributed significantly to their success. In 2011, Massachusetts Institute of Technology (MIT) researchers also published a paper documenting their own work involving OPVs. [454] They proved that oxidative CVD could be used to create conformal conductive polymer electrodes on common paper substrates for the fabrication of OPV circuits.

A team of researchers from MIT, National Tsing-Hua University, Harvard, U.S. Army Research Laboratory (ARL), and Stanford published a paper in 2014 detailing their use of CVD for flexible electronics fabrication. [455] They demonstrated a large-scale electronic system based on graphene/molybdenum disulfide heterostructures grown by CVD. In their devices, molybdenum disulfide is used as the transistor channel while graphene is used as the contact electrodes and circuit interconnects. Their high-performing large-scale devices and circuits prove that CVD is a viable and practical option for flexible electronics.

Most recently, Purdue University released an article in March 2015 detailing their new PECVD process for coating copper nanowires (NWs) with graphene, which leads to more efficient data transfer and thermal management. [456] Their PECVD processes allows the NWs to be coated at lower temperatures, which helps prevent copper oxidation. The hybrid wires are being targeted for transparent and flexible display applications because they are bendable, transparent, and have an increased working life due to the lower levels of copper oxidation.

In the commercial FHE market, it appears that CVD is also mainly used to produce graphene films. In fact, CVD has been identified as the most promising way to grow large, high quality sheets of graphene. [457] Graphenea, a company headquartered in Spain with a U.S. location in Massachusetts, was granted a patent in February 2015 for a method of transferring graphene film. The patent describes a process where graphene is grown with CVD onto a metal foil and

then transferred to an insulating substrate where it would be more useful. Graphenea expects that this method of producing and transferring graphene will be used in electronics applications, including solar cells, batteries, tough screens, display technology, and sensors, among others.

Graphene Frontiers, a privately held company founded in 2011 and headquartered in Pennsylvania, currently has a patent pending CVD manufacturing process for producing graphene at atmospheric pressure, which makes their technology compatible with roll-to-roll manufacturing. [458] After deposition, this process is capable of transferring graphene to nearly any substrate. Graphene Frontiers has created a line of Six™ chemical and biological sensors that consist of a FET with a graphene channel where receptors can be attached. They also anticipate their materials will be used as a transparent conductor and an encapsulating ultra-high barrier film for flexible electronics, including OLED and OPV technology.

BGT Materials Limited, established in 2013 and located in the United Kingdom, creates graphene films with CVD for the flexible electronics industry. [357] Like Graphenea, BGT Materials identifies graphene grown through CVD as an ideal material for flexible electronics applications because it is continuous, ultra-thin, flexible, and highly conductive. Some of the specific applications that they list for their CVD graphene products include e-paper, flexible displays, smart glass, light emitting diode (LED) and OLED lighting, flexible sensors, transparent actuators, batteries, and supercapacitors, in addition to a variety of biomedical applications. Currently on their product list, BGT Materials offers high-quality CVD graphene films, high-mobility graphene FET, high-performance silicon-graphene anode materials for Li-ion batteries, graphene oxide (GO) solution, and graphene ink.

Aixtron, a large German company with 2014 revenues just under 200 million euros, specializes in CVD equipment for the electronics industry. [460, 461] Since 1983, they have produced CVD and ALD equipment for compound and silicon semiconductors. As FHE have grown in popularity, Aixtron has developed systems that are compatible with organic semiconductors and nanotechnology. While still primarily focusing on their flagship technology for the conventional electronics industry, Aixtron is looking to become more involved in the OLED and nanotechnology electronics industries with its new equipment innovations.

While several examples of universities and companies that are investigating or have already commercialized CVD processes for application in the FHE industry can be found, problems still exist that need to be overcome before this technology can become mainstream. [462] First of all, traditional CVD requires operation at extremely high temperatures, which makes it incompatible with leading film substrates that are being considered for flexible electronics. The high temperatures also can cause oxidation on other materials, leading to an undesirable loss of conductivity. Efforts have been made to address these issues, which is where PECVD comes into the picture, but there is still work to be done in this area to ensure that the temperatures are compatible with the substrates and materials of interest. Additionally, CVD is traditionally a vacuum-based process, making it unsuitable for roll-to-roll manufacturing environments. One company discussed above, Graphene Frontiers, claims to have solved this issue by creating a CVD graphene system that operates at atmospheric pressure, but this is not a very widely used technology. Finally, compared to traditional graphics printing processes, CVD is a relatively expensive method of depositing a material onto a substrate. However, for some materials of

interest in the FHE industry, like graphene, this might be one of the best ways to create the high-quality films that are needed for high-performance electronics.

4.1.2.2.2 Atomic Layer Deposition

ALD, sometimes called atomic layer epitaxy (see Section 4.1.2.2.9), was introduced in 1977 to deposit ZnS for flat panel displays. [463] ALD is similar to CVD, and in fact, many ALD procedures were developed from a variety of CVD processes. The ALD process, demonstrated in Figure 17, essentially builds a film layer by layer until the desired film thickness is achieved. In this process, a precursor gas material is introduced into the ALD chamber, and the material reacts with the substrate surface. After the reaction, all of the unreacted precursor gas and reaction by-products are evacuated from the chamber. Then, a second reactive gas material is pulsed into the chamber and reacts with the precursor on the surface of the substrate. These reactions are self-limiting processes so that no more than a monolayer can be formed at the surface within a single cycle. The excess material and by-products are then once again evacuated from the chamber. This process repeats to build up a film layer-by-layer until the desired film thickness is achieved.

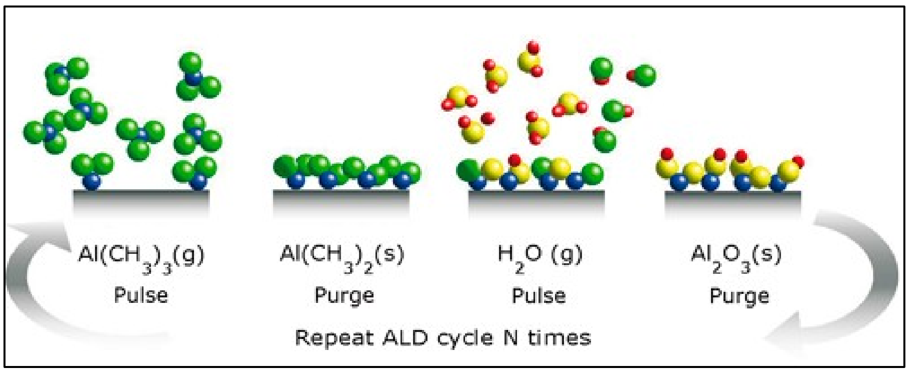


Figure 17. Example of ALD Process [464]

One of the benefits of this process compared to CVD is the operating temperature. [358] Typically, the ALD process is conducted at temperatures below 350 °C, compared to CVD where the substrate could need to be near 800 °C. Because ALD is a self-limiting process that only deposits a monolayer at a time, the resulting films are very conformal and structured. This also allows the film to be customized, in terms of thickness and composition, for the specific application in mind.

However, because of these advantageous features, ALD has extremely slow deposition rates. [463] Significant time is required in the pulsing and purging steps for each cycle, and multiple cycles are used for any particular coating. The time also increases as the substrate surface becomes more intricate since longer pulses are required to ensure material is deposited in the 3D areas of the surface. To address this issue of slow deposition rates, spatial ALD (SALD) was developed. In this variation, the traditional pulse/purge chamber is removed and replaced with a spatially-resolved head or nozzle. This head can either move around the substrate to deliver gas to a specific location, or the head can be stationary with the substrate moving past as it delivers gas to build a film. In chamber ALD, each cycle typically lasts longer than 20 seconds, but with SALD, a typical cycle is 0.05 – 0.2 seconds. [465]

The capabilities of ALD to produce conformal and uniform thin films with precise thicknesses has caught the attention of the FHE industry. ALD processes have been used with increasing frequency for barrier layers and in the encapsulation of both rigid and flexible electronics. A report from several Fraunhofer Institute researchers details the various deposition methods that can be used to apply barrier layers to flexible electronics, and they mention that both Al_2O_3 and TiO_2 barrier layers have successfully been grown in a batch ALD process on low-cost substrates. [466] Low water vapor transmission rates can be achieved with these ALD layers because the ALD process can provide an even coverage of particles and defects on the substrate surface.

They do identify though that traditional ALD has limited productivity because of its slow deposition rates, and that this could be a hindrance for future production.

ALD has also been recognized as a novel method for thin film encapsulation of OLEDs and OPV cells. [467] In 2015, researchers from Jilin University in China published a paper discussing how they used ALD to deposit thin films of Al_2O_3 and Al_2O_3/alucone to create flexible, transparent gas barrier films for flexible optoelectronics applications. Their studies found that hybrid multilayer films that consist of inorganic layers and decentralized organic (in this case alucone) components have much better surface roughness, barrier performance, transmittance, and stability under mechanical deformation than films consisting of pure inorganic layers. They also claim ALD can be used to help enhance these desirable properties.

Some of the same researchers at Jilin University published another paper in 2015 that detailed a low-temperature ALD process that was used to deposit zinc oxide to create flexible transparent electrodes for organic photoelectric devices. [468] In this research, silver NWs were deposited through a spin coating process and then zinc oxide was deposited on top of the silver NW mesh using ALD. This allowed the zinc oxide to fill in the voids in the silver NW mesh and create an extremely conformal coating, leading to continuous contact, efficient charge extraction/injection, and overall improved performance of the modified silver NW electrode.

ALD processes have also been used to demonstrate flexible nonvolatile memory transistors. [469] In 2012, researchers from Hanyang University and Yonsei University in South Korea, and Texas A&M University reported on a low-temperature fabrication method that combined ALD and molecular layer deposition (MLD). MLD is very similar to ALD, but where ALD is used to deposit inorganic materials, MLD is used with organic materials. [470] This combined ALD/MLD deposition process, which allowed for the low-temperature fabrication of organic-inorganic nanohybrid nonvolatile memory transistors, offers new opportunities to develop low-voltage-driven flexible memory electronics fabricated at low temperatures in the future. [469]

Several companies are also invested in the use of ALD for flexible electronics applications, again with a special focus on barrier layers and encapsulation, including ALD NanoSolutions, Lotus Applied Technology, Beneq, Veeco, and Eastman Kodak. ALD NanoSolutions, a privately held company founded in 2001 and headquartered in Colorado, develops state-of-the-art ALD techniques including Particle ALD™, Polymer ALD™, and ALD onto microelectromechanical systems (MEMS)/nanoelectromechanical systems (NEMS) technology. [471] Particle ALD™ produces conformal, uniform, pinhole free, high purity, inorganic nanocoatings on the surface of dry individual particles. This system can be used in flexible electronics applications including

battery systems, improved lighting materials, and low- energy high-sensitivity sensors. Polymer ALD™ is a variant of Particle ALD™ where inorganic nanocoatings are deposited at low temperatures on either polymer particles or substrates. This technique can be used for hermetically sealing OLED devices used to make flexible displays. ALD NanoSolutions has received funding from Defense Advanced Research Projects Agency (DARPA), the National Science Foundation (NSF), the U.S. Department of Energy (DOE), and the Air Force Office of Scientific Research (AFOSR). For example, in June 2011, ALD NanoSolutions received a Phase II Small Business Innovation Research (SBIR) DARPA grant for "Flexible Gas Diffusion Barriers Using ALD/MLD Multilayers and Roll-to-Roll Processing". [472] Today, they identify that their ALD processes can be used for applications including batteries and energy, MEMS/NEMS, and ultra-barriers. [471]

Lotus Applied Technology, located in Hillsboro, Oregon, develops low-cost ALD technology that opens up new opportunities in applications previously not accessible with ALD. [473] Lotus Applied Technology does not manufacture coating equipment, but instead they "deliver their unique technology in collaboration with specialty thin film coating equipment manufacturers". [474] They have conventional pulse-based batch ALD reactors, rotary batch ALD reactors, and roll-to-roll ALD reactors designed specifically for flexible electronics applications. [473] Their rotary systems are intended for hermetic encapsulation and protection for rigid substrates and devices, optical coatings, MEMS, sensors, thin film batteries, and disc and thin film heads. Ideally, Lotus Applied Technology is working to displace conventional ALD in semiconductor processing with their rotary batch ALD reactors. The roll-to-roll ALD systems are suited for the deposition of relatively thin films where high performance, high volume, and low cost are all critical. These systems allow for the continuous deposition of high quality ALD films on flexible substrates at low temperatures and high speeds. [475] This roll-to-roll technology is intended for ultra-barrier films for flexible electronics (including OLED lighting, OLED displays, PVs, electronic paper), high barrier films for commercial packaging (military & emergency packaging, medical packaging, long shelf life food packaging), and functional films for flexible electronics (oxide semiconductors for displays, gate dielectrics for displays and other flexible electronics, transparent conductive oxides (TCOs), antistatic coatings). [473]

Beneq is a company based in Finland that develops production and research equipment for ALD coatings, and is also a manufacturer of thin film electroluminescent (EL) displays. [476] Similar to Lotus Applied Technology, Beneq has ALD equipment for research, batch, and roll-to-roll applications. In addition to flexible electronics, their markets include displays, energy, glass coatings, jewelry, LED & OLED lighting, medical, minting, optics, and solar.

Veeco, a public processing equipment company headquartered in New York, has a Fast Array Scanning Technology ALD (FAST-ALD™) system that is designed specifically for large and flexible substrates. [477] This system operates at low temperatures (>100 °C) and is used to encapsulate flexible OLED technology. Veeco claims that its ALD system is ten times faster than today's commercially available ALD technology, which could solve the slow deposition rate issues characteristic of traditional ALD.

Eastman Kodak, a public printing company headquartered in Rochester, New York, is using ALD in a slightly different way compared to the companies described above. They are making

TFTs using a SALD process to deposit metal oxides for the conductor, insulator, and semiconductor layers. [465] To create these devices, they apply an inhibitor, composed of polyvinylpyrrolidone (PVP), in specific places where they do not want the metal oxide to be deposited. The various metal oxide layers are then deposited through the SALD process, followed by the inhibitor being removed with O2 plasma. The SALD method eliminates many of the concerns of printing, including ink formulation and coffee ring drying. Eastman Kodak believes this technique is ideal in the design stages of development because it allows for the creation of same-day prototype devices, whereas a standard lithography process could take weeks. With Eastman Kodak's initial trials, the mobility values were low and the yield was low. However, they discovered that using a buffer layer and multilayer dielectric helps eliminate some of these issues.

Overall, because of its ability to deposit thin, conformal, and structured films, ALD has been increasingly used in the FHE industry, mainly to deposit barrier and encapsulation layers. However, with Eastman Kodak's recent work, it appears that ALD might be able to do more in the future. One of the main issues that would have to be overcome in order for this to happen would be the slow deposition rates, and SALD appears to be starting to solve this problem. Additionally, as shown by the development of MLD, further research into ALD/MLD for FHE applications should hopefully result in more material options that are compatible with this technology.

4.1.2.2.3 Physical Vapor Deposition

PVD is an environmentally friendly vacuum deposition technique similar to CVD. [478] In PVD, a solid material is first vaporized though various methods, such as high temperature vacuum or gaseous plasma. The vaporized material is then transported in vacuum to the substrate surface, where it condenses into a thin film. The main difference between CVD and PVD, shown in Figure 18, is that CVD involves reactions where PVD simply involves phase changes.

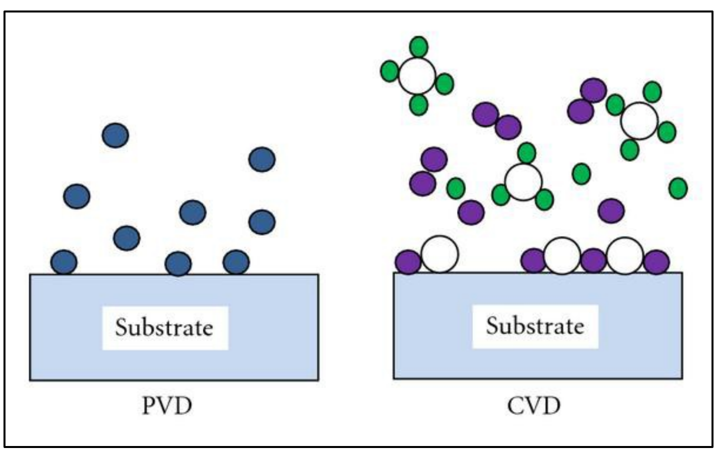


Figure 18. Comparison of PVD and CVD Processes [479]

Several deposition techniques fall underneath the PVD umbrella, including cathodic arc deposition, evaporative deposition, PLD, ion plating, and sputter deposition. [480] These techniques will be discussed in more detail in subsequent sections.

PVD is compatible with a variety of different substrates and surfaces finishes. [481] A large number of inorganic and some organic materials can be deposited through PVD processes. These

two factors make PVD a versatile deposition method, especially since many different versions of PVD can be utilized, as mentioned above. Unlike CVD, PVD processes do not produce any harmful byproducts, making the process environmentally friendly. PVD coatings can also be harder, more corrosion, abrasion, and high temperature resistant, and have better impact strength than coatings applied by other deposition processes.

While PVD generally operates at lower temperatures compared to CVD, PVD processes can still require relatively high temperatures and vacuums, which leads to high costs and necessitates specially trained personnel. [481] Most PVD coating techniques function through line-of-sight transfer, making it difficult to provide conformal coatings to substrates with complex geometries on their surfaces. [482] However, some PVD processes exist to attempt to combat this issue.

Finally, PVD coatings are typically thinner than CVD coatings, and whether that is an advantage or disadvantage is dependent on the particular application of interest.

It appears that the basic PVD process is not referenced often in the FHE industry, and instead the specific types of PVD mentioned above are used more frequently. How these specific variations of PVD are used within the FHE industry are discussed below in their individual sections.

Alternately, a hybrid physical-chemical vapor deposition (HPCVD) process has become more popular as a way to incorporate conventional PVD processes into flexible electronics. This process involves chemical decomposition of precursor gas and physical evaporation of bulk metal at the same time to deposit a thin film on a substrate. [483] In 2007, a team of researchers from The Pennsylvania State University published a paper describing this HPCVD process being used to deposit crystalline magnesium diboride onto thin flexible yttrium-stabilized zirconia substrates for applications in superconducting digital circuits and coated conductor wires. [484]

4.1.2.2.4 Sputtering

Sputtering, a type of PVD, involved a non-thermal vaporization method where surface atoms of a material are physically ejected (vaporized) from a solid target surface by momentum transfer from atomic-sized energetic bombarding particles, which are usually gaseous sputtering ions accelerated from a plasma or an ion source. [485] These vaporized particles from the target source material are then deposited onto the intended substrate. There are many variations of this technique, including ion beam sputtering, ion-assisted sputtering, reactive sputtering, gas flow sputtering, and magnetron sputtering. [486] Magnetron sputtering is typically considered the most common type of sputtering, mostly because its high sputtering rates allow reactive deposition of compound films. [487]

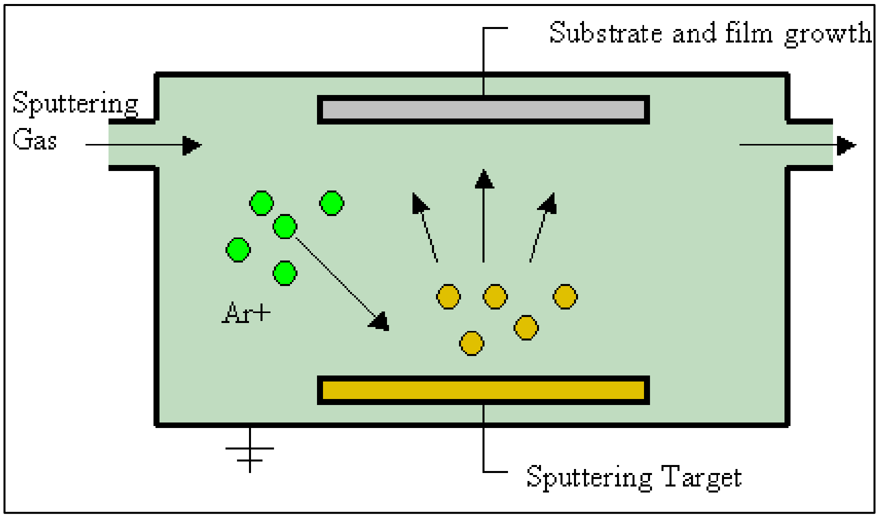


Figure 19. Simple Sputter Deposition Process [488]

Sputtering allows for the deposition of a wide range of materials, even materials with extremely high melting points. [488, 487] The adhesion of the material to the substrate is greater with sputter deposition than it is with evaporation methods. The maintenance of the system is low because the solid source target surface contains a large amount of stable material that does not have be replaced often, which is highly desirable for ultrahigh vacuum applications. Sputtering systems in general have a relatively small footprint and produce very little radiant heat during the deposition process.

Similar to ALD, sputtering unfortunately has relatively low deposition rates compared to other methods such as CVD and evaporation, and the films that are deposited are often non-uniform in both thickness and composition. [487] In some cases, gaseous contaminates in the plasma make their way into the system and are incorporated into the deposited coating. While the solid source target mentioned above is stable and requires little maintenance, it is very expensive, and therefore could necessitate significant initial investment.

Despite the various disadvantages, the advantages discussed above that are offered by sputter deposition cause it to be used in a wide range of applications, including IC manufacturing, coatings on architectural glass, antireflective coatings for optical applications, magnetic films, hard coatings on tools and engine parts, as well as decorative coatings. [485, 488] In addition to these applications, sputtering is also used in the FHE industry, primarily to deposit oxide layers, but it is occasionally used to deposit conductive layers as well. The following paragraphs will highlight a few research groups that are using sputter deposition techniques for FHE, particularly for transistors, solar cells, and transparent electrodes.

Researchers from the New University of Lisbon in Portugal published a paper in 2008 discussing their use of radio frequency (RF) magnetron sputtering to deposit active oxide semiconductor and electrode layers on a paper substrate, which also doubled as the dielectric layer, to create high-performance flexible hybrid field-effect transistors [489]. They felt that transistors processed through room temperature sputtering techniques had enhanced performance both initially and after letting the devices sit for two months, and actually had performance that rivaled devices processed at higher temperatures.

A team from the University of Strasbourg in France presented at a conference, in 2012, regarding work they had performed with sputtered solar cells. [490] Their associated paper describes the interest in zinc oxide as an interfacial buffer layer in organic solar cells. They demonstrate that high quality zinc oxide films can be prepared on large-area ITO-coated flexible substrates using low temperature sputtering, and they claim that their low temperature sputter deposition technique is compatible with roll-to-roll manufacturing.

In 2013, two researchers from Arizona State University published a paper describing using a sputtering process to create transparent electrodes. [491] In their work, multilayer structures of $TiO_2/Ag/TiO_2$ were deposited one at a time onto flexible substrates using room temperature sputtering, resulting in the formation of an indium-free transparent composite electrode. Their process can be conducted at room temperature, and does not require a post-annealing process, allowing for the use of temperature sensitive substrates characteristic of the flexible electronics industry. They expect that their transparent electrodes could be used in solar cell or display applications.

Several companies produce sputtering equipment for the electronics industry, and some of them are even focused specifically on flexible electronics with roll-to-roll sputtering systems. Kobelco, a Japanese steel company, has a sputter roll-to-roll coater that can deposit TCO, optical coating, and metallic coatings for applications in the flexible electronics and energy industries [492] Their systems, which can meet the needs of both development and production environments, have been used for touch panels, PV cells, window film, and flat panel displays. They can also incorporate pre-treatment functionality through ion beam or plasma irradiation to improve the adhesion of the coating to the substrate. The compatible substrates with these systems include plastics, flexible glass, fabrics, and metal foils.

Deposition Technology Innovations (DTI), a privately owned company in Indiana, also has roll-to-roll sputter coating systems. [493] Since their foundation in 2009, they have offered sputtering and EB evaporation services that are applicable in the flexible electronics, alternative energy, solar control, and specialty products markets. Specifically regarding their sputtering technology, DTI offers toll roll-to-roll sputtering services on flexible substrates. Their product development facility includes a full production size sputter coater, clean room slitting, and rewinding capabilities.

While they do not specifically mention flexible electronics as one of their application areas, Semicore, based in California, also offers in-line sputtering systems for production and development environments. [494] Their systems can accommodate a wide range of substrate materials, including plastic films, glass, ceramics, metals, and hybrids, and are intended for the electronics, academic, optical, solar energy, medical, automotive, military, and high technology industries.

Sputtering seems to be prevalent in the FHE industry, but generally only in niche areas, such as for the deposition of oxide layers. Perhaps the technology's shortcoming is its tendency to have inconsistent film thickness and composition, which is definitely not desirable in the electronics industry. However, with such a large number of commercial systems already compatible with

roll-to-roll production and low temperature environments, it would not be surprising if sputtering became a more prominent deposition technique for FHE in the future.

4.1.2.2.5 Evaporation Deposition

Vacuum evaporation, sometimes also referred to as vacuum deposition or evaporation deposition, is another type of PVD. This deposition process, which is depicted in Figure 20, involves heating a source material within a chamber under vacuum until it evaporates, and then allowing the evaporated particles to move around the chamber and condense on various surfaces. [495] Being under a vacuum during this process allows the particles to evaporate freely within the chamber and move around without colliding with background gases, and also helps to help eliminate some contaminant gases that normally would be present without a vacuum.

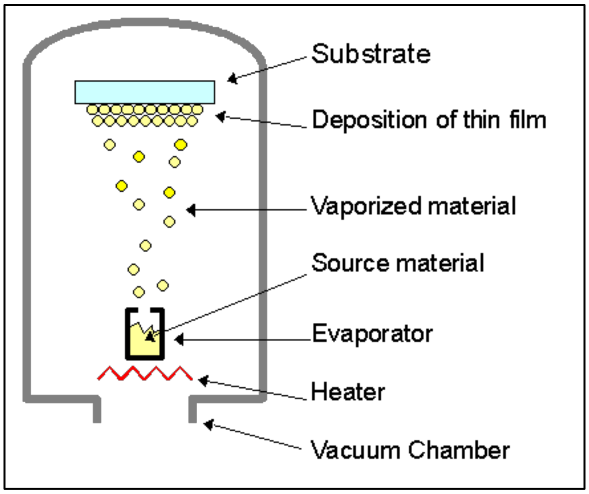


Figure 20. Evaporation Deposition [496]

Several different variations of evaporation deposition exist, and they are defined by the energy source that is used to evaporate the deposition material. The source can be thermal, where the deposition material is heated by ceramic evaporators that are shaped like boats that hold melted material. [497] The material can also be heated with an EB, where the EB is aimed at the source material to cause local heating and evaporation. [495] EB heating often involves dangerously high voltages, so these systems require extra safety features. [498] Resistive evaporation can be used, where a tungsten boat containing the source material is electrically heated with a high current to cause the material to evaporate. [495] Resistive heating often has less safety issues because although the current is high, the voltage applied is very low. [498] The type of energy source chosen is dependent on various attributes of the entire system, including what type of material needs to be evaporated, what type of quality the finished coating needs to have, and how fast the deposition needs to occur.

Evaporation deposition is a line-of-sight deposition method, which has advantages and disadvantages depending on the intended application. [485] This feature could be beneficial because it allows for the use of masks to define only certain areas for deposition and enables patterning capabilities. However, line-of-sight deposition leads to poor surface coverage and uniformity, especially on surfaces with complex geometries. This could require elaborate tooling and device configurations in an attempt to evenly coat all desired surfaces.

Evaporation deposition as a whole is relatively inexpensive compared to other PVD techniques. [485] Vacuum evaporation has characteristically high deposition rates, and these systems can be configured with various hardware and software options that allow real time deposition rates and thickness to be easily monitored. [485, 498] Vacuum evaporation systems are versatile and are compatible with many forms of source material, including chunks, powder, wire, chips, etc. [485] The source material typically has high purity and is relatively inexpensive.

In addition to the line-of-sight issues mentioned above, vacuum deposition has a few other disadvantages. Several desirable alloys and compounds are not compatible with this system. [485] Additionally, since thermal evaporation is at the heart of this technique, high radiant head loads are often seen during processing. Using an EB source definitely helps this though, as the heating is much more direct and efficient compared to thermal or resistive heating sources. [359] While there can be real time monitoring of deposition rates and thickness, actually controlling the deposition is difficult to achieve. Typically, all surfaces within the chamber, not just the desired surfaces, are coated with the deposition material, which leads to a poor utilization of resources. [485] Unfortunately, as a trade-off to high deposition rates, poor qualities are often found in the deposited films, such as pinholes, contaminants, and non-uniform thicknesses across the entire surface.

Evaporation deposition is used to create coatings for optical, decorative, and protective purposes, barrier films for flexible packaging materials, and electrically conducting films for the electronics industry. [485] Some of these applications, such as barrier films and conductive films, can also be used in the FHE industry. Examples of where evaporative deposition has been used for flexible electronics will be described briefly below.

In 2005, a student at Louisiana State University wrote a Master's thesis on thermally evaporated pentacene thin films. [500] The report described TFTs that were created in bottom contact structure using a thermal evaporation method to deposit pentacene as the organic semiconductor material. Other possible deposition methods for organic polymers are mentioned, including molecular beam deposition, spin coating, organic vapor phase deposition, and screen printing, but thermal evaporation in vacuum was described as "ideal for depositing pentacene", though specific reasoning was not provided. It was discovered that the deposition rate and the purity of the source material for the evaporation process significantly affects the crystallinity and structure of the deposited films.

Researchers at University of Cincinnati and the U.S. Air Force Research Laboratory (AFRL) also created pentacene TFTs using an evaporation deposition method. [501] In February 2014, they published a paper describing their work to create pentacene organic thin film transistors (OTFTs) on paper substrates using a dry-step process. This all dry-step process included vacuum evaporation and shadow masking techniques. They were interested in this type of deposition system because it offered the ability to perform simple patterning techniques without needing to expose the substrates to the liquids involved in conventional photolithography, which is desirable when paper substrates were involved. The goal of the study was to compare OTFTs on paper substrates to OTFTs on liquid crystal display (LCD) glass and flexible glass substrates. They found that even though the performance of their vacuum evaporation devices was low compared to devices created through more complex fabrication processes, the results were promising and

provided a good start for flexible electronics created on paper substrates with simple manufacturing techniques.

Shortly thereafter, another research team published a paper in August 2014 describing organic digital logic and analog circuits that were fabricated in a roll-to-roll compatible vacuum evaporation process. [502] The circuits and devices they created on their roll-to-roll evaporation system include inverters, NAND and NOR logic gates, simple memory elements, a modified Wilson current mirror circuit, and OTFTs. While the ideal performance for some of the circuits has not yet been achieved with this technique, the ability of this evaporation process to create reproducibly high yields of stable devices will allow for the design and production of more complex circuits and devices as more research is conducted. Additionally, the roll-to-roll compatibility of the system will make it extremely desirable as the FHE industry grows.

In addition to being able to deposit semiconductor layers like pentacene, evaporation deposition methods have been used to apply conductive films for flexible electronics applications. In March 2015, researchers at the Gwangju Institute of Science and Technology in South Korea published a report describing polymer-metal hybrid transparent electrodes that could be used in flexible electronics. [503] Their flexible transparent electrode consists of a silver layer sandwiched between two different polymer layers. Various layers of the electrodes, including the conductive silver layers, were deposited through vacuum evaporation techniques. These electrodes were used to make polymer solar cells and polymer LEDs. Several steps in the solar cell and LED device fabrication process also utilized vacuum evaporation deposition techniques.

Outside of depositing functional layers, such as semiconducting and conducting films, for flexible electronics, evaporation deposition can also be used to deposit barrier layers, similarly to how it is used for conventional electronics manufacturing. A research team consisting of members from the National Physical Laboratory in India and the Indian Institute of Technology Delhi published a paper in 2011 detailing organic thin film encapsulation techniques for OLEDs. [504] The organic materials that comprised the encapsulating layer were deposited by a simple vacuum thermal evaporation technique, and the resulting encapsulation is ultrathin, transparent, and applicable for use in flexible and top emitting OLEDs. As part of their studies, they found that evaporation deposited organic films showed acceptable barrier properties and the encapsulation layer significantly slowed down oxygen and moisture diffusion into the device.

Since evaporation deposition is such a well-known and widely used deposition technique, especially in the electronics industry, there are many companies that produce, use, and sell evaporation deposition equipment into various industries. Some of these companies include BOBST Manchester Ltd. (United Kingdom), Darly Custom Technology, Inc. (Windsor, Connecticut), Denton Vacuum, LLC (Moorestown, New Jersey), Kurt J. Lesker Company (Jefferson Hills, Pennsylvania), Vergason Technology, Inc. (Van Etten, New York), Dynavac (Hingham, Massachusetts), and Johnsen Ultravac, Inc. (Ontario, Canada). [505, 506]

A couple companies slightly more involved in the flexible electronics industry include Semicore and Angstrom Engineering. Semicore, mentioned above in Section 4.1.2.2.4 for their in-line sputtering systems, does not explicitly say they are involved in flexible electronics, but their name comes up frequently when researching various deposition methods for flexible electronics.

[494] In addition to sputtering systems, Semicore also offers in-line thermal evaporation and EB evaporation systems. In fact, their Tri-AxisSM product is a system designed for R&D and small batch production environments that incorporates sputtering, evaporation, and PVD capabilities within a single system. It is designed to handle materials and hybrid substrates used in the electronic, optical, solar energy, medical, automotive, military, and aerospace industries. Angstrom Engineering, located in Ontario, Canada, has custom-designed PVD machines that are used in renewable energy, organic electronics, flat panel display, magnetic storage, decorative coatings, photonics, spintronics, quantum dots, and various optical and tribological applications. [507] They have systems capable of resistive thermal evaporation, sputter deposition, EB evaporation, and ion assisted deposition (IAD), as well as custom process capabilities.

Advantech US, headquartered in Pittsburgh, Pennsylvania, is one of the only companies developing evaporation deposition techniques specifically for the flexible electronics industry. [508, 509] They have created AMAX Evaporation Printing™, a vacuum deposition system for manufacturing microelectronic devices using an additive manufacturing technology that performs in-line material deposition through shadow masks with precision alignment and feature sizes down to five microns. Their system is compatible with both rigid and flexible substrates and a variety of bulk deposition materials, and has demonstrated potential for chip packaging, microelectronic devices, circuitry, ePaper display backplanes, and OLED display front panels.

From the examples provided, it appears that evaporation deposition is used in a variety of areas within the flexible electronics industry, from depositing conductive films to semiconducting materials to encapsulation layers. And with the AMAX Evaporation Printing™ technology from Advantech US, it can be expected that this deposition technique will become even more prominent, especially since their systems can achieve levels down to five microns. The biggest hindrances for evaporation deposition will most likely be its line-of-sight characteristics and its inability to produce highly uniform and defect free films. Unless Advantech US or others address these issues, vacuum evaporation will not be as strong of a player when high performance is needed or complex geometries are involved. However, many already existent applications in flexible electronics simply require the deposition of a consistent material over a large flat surface, and this is where evaporation deposition could possibly excel in the future.

4.1.2.2.6 Pulsed Laser Deposition

PLD is a PVD technique that uses a pulsed laser to deposit material onto a substrate. [510] In this deposition method, which is shown in Figure 21, high power pulse lasers are used to melt, evaporate, and ionize material from the surface of a target. This produces a plasma plume that expands and travels away from the target surface, and then condenses and deposits as a thin film on an appropriately placed substrate. The deposited film has the same chemical composition as the original target material. [511] The process can occur in ultra-high vacuum or in the presence of a background gas such as oxygen, which is typically the case when depositing oxides. [512]

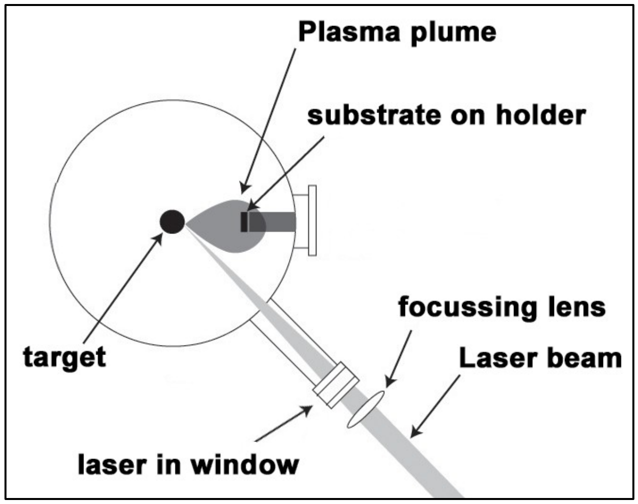


Figure 21. PLD Process [512]

While visible and infrared (IR) lasers can be used for PLD, UV beams are most often found in PLD systems. [513] Within UV pulsed lasers, high energy lasers provide several benefits for PLD, including increasing the number of materials that can be deposited with these systems. It also allows a larger area of the source target to be vaporized, which increases the deposition rate and efficiency.

One of the main benefits of PLD is, as mentioned above, the consistent composition between the deposited film and the target source material. [510] PLD systems also have relatively high deposition rates, and the film thickness can be controlled in real time.

Unfortunately, both the thickness and the composition of the deposited film can vary greatly across the substrate. [510] The maximum area of the substrate that is capable of being deposited with material is also small. PLD techniques are used in a wide range of industries, from electronics to medical devices, but despite this, the process itself is not widely understood. [510] Therefore, a significant amount of upfront research and optimization is required in order to efficiently use a PLD system, and PLD has become an increasingly popular topic in academic research communities.

PLD has been used in the FHE industry to deposit insulator, semiconductor, and conductive layers for a variety of applications. In 2004, a team of researchers from Tokyo Institute of Technology published a report where they described a room temperature fabrication method for producing transparent, flexible TFTs. [514] In this method, they utilized PLD to deposit amorphous oxide semiconductor and the ITO conductive layer to create the TFT. This method was performed at room temperature, which allowed them to use inexpensive polymer films as the substrate. They do mention however that even though they utilized PLD in their work, sputtering or CVD techniques could be used for large area uniform deposition and mass production, areas where PLD tends to fall short.

Besides amorphous oxide semiconductors, PLD can be used to deposit other types of semiconductors onto flexible electronics substrates. Researchers from University of Wollongong in Australia published work that they performed in 2010 to create flexible anodes for lithium ion

batteries. [515] They were able to successfully deposit silicon onto SWCNT paper in order to create a silicon/SWCNT composite paper that was used as an anode material in battery applications.

PLD has also been demonstrated to be useful for photonics and optoelectronics applications. A team from Bowling Green State University and University of Toledo reported on findings in 2007 regarding CdS semiconductor films. [516] According to their research, CdS films were deposited onto transparent plastic foil substrates using PLD. While it is not clear whether these properties were a function of the material, process, or both, they reported that their experiments resulted in films that had low surface roughness and good adhesion to the flexible substrates. Unfortunately, the only details given in this work regarding the end use of these materials was that they were intended for "photonic applications". More examples of PLD being used for photonics/optoelectronics applications were published in 2011 in a book chapter written by Ullrich Bruno at AFRL. [517] In this chapter, he provides several examples of materials, including CdS and GaAs, which were deposited through PLD methods in order to create optoelectronic devices. Specifically, he discusses how low temperature PLD processes are ideal for the production of device prototypes, such as the GaAs-on-glass merger and GaAs/Si photodiodes.

An example of how PLD can be used to deposit conducting layers is provided in a paper published in 2010 regarding research performed by scientists at West Virginia University and University of Birmingham (United Kingdom). [518] In their work, PLD was used to deposit high-quality ITO thin films on PEN flexible display substrates. They investigated the effects of background oxygen gas, when is typically used when depositing oxides, on various qualities of the deposited films, and they were able to optimize the system to determine a range of oxygen gas pressures that resulted in the best electrical resistivity and optical transmission values. Countless companies exist today that produce PLD equipment, and a report published in 2014 by PVD Products, Inc. concisely describes the history of PLD technology and equipment and the current state-of-the-art for commercial PLD equipment for both laboratory and production environments. [519] This report goes into detail about the various companies that produce PLD equipment, including PVD Products, Inc. (Wilmington, MA), SVT Associates, Inc. (Eden Prairie, MN), Blue Wave Semiconductors (Baltimore, Maryland), and Coherent (Santa Clara, CA). For more information on PLD equipment, see PVD Products' report. [519]

One company was identified that has developed a PLD system specifically for flexible electronics. [520] A press release from March 2014 identified that Picodeon's ultra-short PLD system could be used to apply aluminum oxide coatings to heat sensitive plastic electronics, such as OLED screens, as an encapsulation and barrier layer. They claim that the ultra-short pulses from the laser are low enough to not damage or warp the substrates. In this press release, they mention that they will further develop other coatings that can be used in the flexible electronics industry as well, such as silver, copper, and tin oxides.

Most companies that sell PLD equipment, including the ones listed above, have other deposition technologies in their portfolio as well. These companies also supply PLD equipment to several different industries, not just FHE. In fact, some of them only mention electronics as an application area for their equipment, not specifically FHE. However, it is not a stretch that this

equipment would be used for the flexible electronics industry because, as noted by James Greer [519], PLD is a low temperature process when compared to other PVD techniques and therefore is compatible with temperature sensitive substrates used in the FHE industry.

As demonstrated by the examples above, certain areas of the FHE industry are in fact utilizing PLD techniques. This trend makes sense because it has high and controllable deposition rates, and is compatible with low temperature processing. However, because it is a deposition method that is not completely understood, it appears to be much more popular in the academic world of flexible electronics than it is in the commercial world at this moment. Perhaps with Picodeon's new capabilities leading the way, PLD will become a more prominent deposition technology for the FHE industry in the future.

4.1.2.2.7 Ion Plating

Ion plating, also called IAD, ion vapor deposition (IVD), or ion beam assisted deposition (IBAD), is a PVD technique that utilizes either concurrent or periodic bombardment of a substrate by both the desired deposition material and atomic-sized energetic particles (ions). [485] Typically, ion bombardment can be performed before deposition occurs in order to clean the substrate surface. [521] Then, ion bombardment is continued throughout the deposition process in order to modify and control the properties of the depositing film (such as morphology, density, stress level, crystallinity, and chemical composition [522]), as well as to ensure that an atomically clean interface is maintained. Specifically, the bombarding energetic particles clean the surface by removing water and hydrocarbons, densify the growing film, remove loosely bound molecules during film growth, increase the deposition growth rates, and increase the reactivity of the reactive gas, if applicable. [523] Overall, the ion bombardment helps to increase the adhesion of the deposition material to the substrate and increase the quality of the deposited film.

The depositing material can be vaporized by a variety of sources, including thermal evaporation, sputtering, arc erosion, and decomposition of a chemical vapor precursor, but typically an EB gun is used. [485, 524] The energetic particles can be inert or reactive, where reactive particles would allow for multimaterial films or films of compound materials to be deposited.

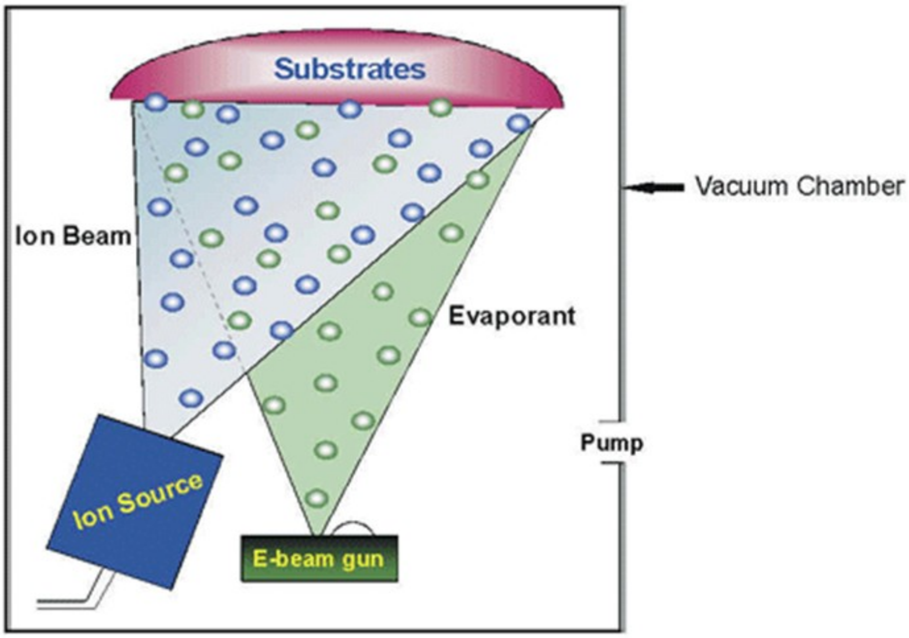


Figure 22. IAD Deposition Technique [524]

As mentioned, this process allows for increased adhesion and improved film quality with regards to several different aspects. However, ion plating is expensive because of the equipment and the large number of processing variables that need to be controlled. [487, 525] Additionally, the substrate can experience excessive heating, which could be detrimental to many films used for FHE. [487] Deposition rates are also relatively low for this process compared to others. [525]

Because of the high quality and increased adhesion that is typical of this process, ion plating is often used for optical applications, specifically to deposit multilayer optical interference coatings for optical filtering and antireflection. [524] It can be used to deposit hard coatings of compound materials on tools, adherent metal coatings, and conformal coatings on complex surfaces. [485] Ion plating can be used for flexible electronics applications as well, and a few examples are described in the following paragraphs.

At Northwestern University, Dr. Tobin J. Marks' research group is highly involved in organometallic chemistry, molecular photonics, transparent oxides, and molecular electronics. Within his transparent oxides group, a main area of focus is on IAD, specifically regarding film growth mechanisms and novel oxide films for electronic device applications. This group has been successful at depositing conducting, semiconducting, and insulating films with IAD methods, even on organic and plastic substrates at room temperature. In 2006, researchers from Professor Marks' group at Northwestern University published a paper describing their successful fabrication of high-performance transparent inorganic-organic hybrid thin film n-type transistors. [526] For their process, they grew the inorganic oxide semiconductor layer using IAD while they used a self-assembly process for the organic dielectric layer. This allowed for a high-mobility transparent inorganic semiconductor layer and an ultrathin high capacitance gate dielectric that resulted in a completely transparent transistor.

In 2007, researchers from Purdue University, Northwestern University (including Dr. Marks), and University of Southern California published a paper describing their fabrication method for fully transparent NW transistors. [527] The gate electrodes on these NW transistors, which can be used in transparent flexible electronics applications, were produced through ion-assisted deposition at room temperature. The team expects that this technology can be used in future display applications.

Xlim Research Institute at the University of Limoges in France is also looking into ion plating technology. [528] Within the institute, one of the research focuses is on plastic optoelectronics, including OLEDs, OFETs, and OPVs. They have identified IBAD as one of their specific technologies of interest within the plastic optoelectronics group, specifically with regards to being able to deposit metallic cathodes. However, published papers regarding their work in this area could not be found.

Some companies that produce other types of deposition equipment, including companies that are mentioned above and below, also produce equipment with IAD capabilities. Many of these companies have IAD as an additional option on their existing equipment, which provides customers with the opportunity to increase adhesion and quality of their deposited films. A large majority of these companies are involved in a variety of markets, including optics, semiconductors, electronics, and "emerging technologies", but most of them do not specifically mention the FHE industry. A few examples of companies that produce IAD systems or IAD films include Intellivation (Fort Collins, CO), Veeco (Plainview, NY), OptoSigma (Santa Ana, CA), and Denton Vacuum (Moorestown, NJ).

DTI, which was mentioned above for their sputtering and evaporation capabilities, has recently added IBAD to their technology portfolio, with intentions for application in various markets, including the medical field, flexible electronics, and specialty products. [529] With this technology, DTI is capable of depositing metals (silver, titanium, gold, platinum, and nickel) and ceramics (titanium nitride, aluminum nitride, silicon dioxide, aluminum oxide) onto plastic, metal, and nonwoven substrates.

Overall, ion plating deposition is a technique that can be used in FHE applications when extremely high quality and performance is necessary. It appears that Tobin Marks' group at Northwestern University has been invested in this area since at least 2006, and according to his research group website, he seems to still be researching it heavily. IAD is already widely used in the optoelectronics field, and could possibly continue to be used as those devices become more flexible, as long as the high processing temperature issues can be overcome.

4.1.2.2.8 Electrospray Deposition

Electrospray deposition is a method of transforming a liquid into a fine mist through atomization by electrical forces, and then depositing that mist onto a substrate. [530, 531] A high voltage is applied to the atomizer nozzle, typically a metal capillary, and the established electric field puts stress on the liquid surface. [531] The stress causes elongation of a jet of liquid and eventual disintegration into droplets that range in size and can be as small as a few nanometers. The tiny particles are attracted to a counter-electrode by electrostatic force and are deposited onto the

substrate. [530] Various patterns in the deposition layer can be produced through masks or additional electrodes.

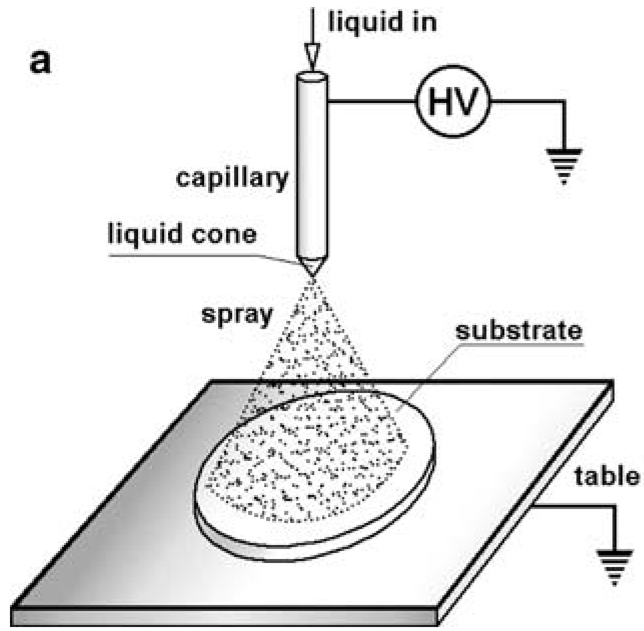


Figure 23. Electrospray Deposition Technique [531]

This method can deposit various inorganic and organic materials, including biomolecules, synthetic polymers, and nanostructures. [530] Because macro-molecular materials, such as polymers and biomolecules, cannot be easily evaporated, it is difficult to use other deposition methods like PVD, PLD, evaporation, or sputtering to create thin films of these materials. [532] Therefore, electrospray deposition is ideal for these types of materials because evaporation is not required as part of the process. Electrospray deposition can be performed at room temperature and atmospheric pressure, potentially eliminating damage to the deposited materials and substrates and safety hazards. [530] Electrospray processes are simple, cheap, flexible, and easily controllable, and they produce homogeneous films of low porosity on large areas at relatively high growth rates. [531] They are also extremely efficient because at least 80 percent of the material sprayed is deposited onto the desired substrate.

Despite all the advantages and all the research that has been conducted, electrospray mechanisms and the film formation processes are still not completely understood, similar to PLD. [531] For example, researchers have noticed that if the substrate temperature is too low, cracks can be formed because the solvent does not evaporate fast enough. However, if the temperature is too high, the solvent evaporates too quickly, and the particles are deposited as solids, leading to a very porous layer. Additionally, electrospray methods are very sensitive to the properties of the material being deposited. Therefore, much more research and optimization needs to be performed on electrospray deposition.

Since 2012, there have been countless examples of electrospray deposition techniques being used by researchers for FHE applications, such as PVs and lighting. Below are short descriptions of some research groups using this method and the devices that have been created. This method is often used to deposit organic materials that cannot as easily be deposited by other high

temperature techniques, such as polymers like poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) or carbon nanotubes (CNTs).

In January 2012, a team from Sungkyunkwan University in South Korea published work they performed utilizing electrospray deposition methods [533]. In their research, they were able to deposit polymer thin films for applications in OLEDs. They found that their devices were able to achieve performance comparable to devices created through spin coating processes, which is a widely used technique for polymer deposition. In September 2013, some of the same researchers at Sungkyunkwan University published another paper on electrospray deposition. [534] This time, they were fabricating flexible transparent CNT electrodes on a large area. The electrode films showed high flexibility and transparency, making them compatible with solid stage lighting, touch panel, and solar cell applications.

Researchers from Gwangju Institute of Science and Technology published a report near the beginning of 2012 detailing their use of electrospray deposition techniques to deposit highly conductive polymer films. [535] They optimized their spraying conditions in order to fabricate a PEDOT:PSS electrode for a semitransparent inverted organic solar cell. Using this method, they did not incur any damage, and therefore no performance degradation, to the underlying photoactive layer.

In June 2012, a team of researchers from University of Camerino (Italy), Johannes Kepler University Linz (Austria), Universite Bordeaux (France), and COMSATS Institute of Information Technology in Pakistan published an article describing their work to create organic solar cells through electrospray deposition. [536] Specifically, they used the electrospray process to create the active layers in the solution processed organic solar cells. The electrospray technique allowed them to use low concentration solutions, which enables polymers or other materials with low solubility to be candidates for future devices.

Similarly, in January of 2013, researchers from Saitama University in Japan researched electrospray deposition as a method to deposit thin films of three different fullerene derivatives. [537] In their work, they observed how various deposition variables, such as spray diameter and supply rate, affected the quality of the thin film and the performance of the overall device. As a result, they were able to create OPV devices by depositing thin films of organic semiconductor nanoparticles through electrospray techniques.

Despite the multitude of research articles about electrospray deposition that can be found, very few companies that produce or use electrospray equipment were identified, and none of them produce equipment specifically for the FHE industry. In fact, several of the electrospray systems described in the various articles above are experimental systems that were fabricated by the researchers for use in their experiments. Overall, three companies were identified that produce and/or use electrospray equipment. Toray Engineering Co., Ltd., located in Japan, has an electronic spray coater that can produce high-precision thin film for OLEDs, touch panels, and solar cells, among others. Fuence Co., Ltd., also located in Japan, has several series of electrospray deposition equipment. They have product lines targeted for R&D and small-scale production, as well as large-scale high-speed production. MolecularSpray, headquartered in the United Kingdom, manufactures ultra-high vacuum compatible electrospray deposition systems.

Their systems are used in university and industrial R&D settings to deposit complex, fragile, and non-volatile molecules on surfaces under ultra-high vacuum conditions.

It can be seen that this deposition technique has become quite popular within the last decade for flexible electronics applications. This is mainly due to its ability to deposit macromolecular and non-volatile species, which is important as organic electronics become more prominent. However, it appears that most of the work involving electrospray deposition is being done in the academic sector, and industry is still focused primarily on other deposition methods for the time being. In order for electrospray deposition to work in nanoelectronics applications, it will be necessary to develop direct patterning techniques that can achieve pattern sizes below one micron. [531]

4.1.2.2.9 Epitaxy

Epitaxy is a type of CVD process where a crystal is grown on top of another crystal. [538] The orientation of the grown crystal is determined by the orientation of the underlying substrate crystal, which is demonstrated in Figure 24. If the material being grown has the same composition as the substrate material, the growth is called homoepitaxy. If the deposited crystal and the substrate crystal are different materials, the process is called heteroepitaxy.

The crystal films can be grown from gas, liquid, or solid precursors, but growing from the vapor phase is most common. [538] In vapor phase epitaxy, deposition precursors are vaporized, and then react with the hot substrate surface. This leaves behind the desired deposition material as a thin film and releases byproducts and unused precursor material. In liquid phase epitaxy, layers grow from a liquid precursor source at a liquid-solid interface. During solid phase epitaxy, a thin amorphous film layer is deposited onto the crystalline substrate, which is then heated to convert the film into a crystalline structure layer-by-layer through atomic motion and recrystallization at the substrate-amorphous material interface.

Epitaxy is primarily used in electronics fabrication to deposit silicon, typically to produce silicon on insulator (SOI) substrates, and for optoelectronics purposes. [449] It is also an emerging process technology for MEMS and nanotechnology applications. In general, epitaxy is the only affordable method of high quality crystal growth for many semiconductor materials. [539]

Because of the many different variables within an epitaxy system, such as homo or hetero deposition and vapor or liquid sources, several versions of epitaxial deposition exist. One of these is molecular beam epitaxy (MBE), a specific type of vapor phase epitaxy, which provides a pure steam of atomic vapor by evaporating a source material. [538] Because it employs (non-reactive) evaporation techniques, MBE is technically considered a non-CVD epitaxial process. [540] In this technique, the evaporated particles travel through a very high vacuum environment to the substrate, where they condense and grow in a specific crystalline orientation.

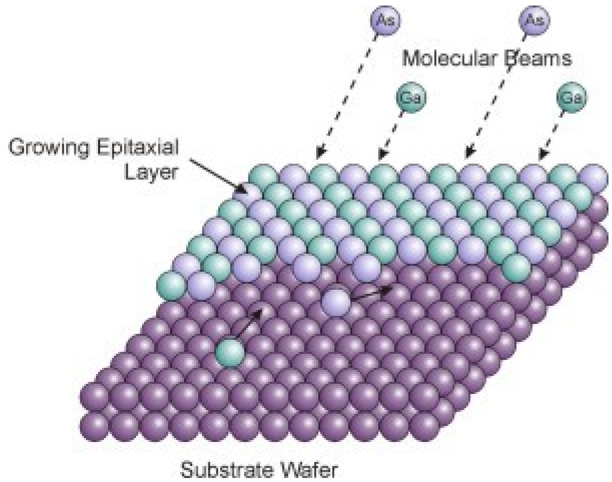


Figure 24. Epitaxial Deposition [541]

The MBE process has been around since the 1960s, but it had not been considered as a suitable technology for silicon device fabrication until recently because the quality of deposited layers was not as high, and acceptable industrial equipment did not exist. [540] Today, equipment is now available, but the quality is still not as high as other epitaxy techniques. It also has low throughput and is an expensive process because of the necessary high vacuum environment. However, MBE does have a few advantages. It is a low temperature process, which makes it more compatible with substrates used for FHE. The process also allows for precise control of doping and complex doping profiles. Layer thickness can also be highly controlled with MBE, and because the growth rate is slow, extremely thin layers can be reliably produced. [541]

MBE is widely used with compound semiconductors, specifically for growing III-V semiconductor crystals, and can even be used to deposit some types of organic semiconductors. [539, 542] Because of its slow growth rate, MBE can produce complex structures of varying layers, which is useful in the production of high-speed transistors, LEDs, solid state lasers, and other high-performance devices. [2]

Since these epitaxy methods are commonly used for semiconductor deposition, it is common for dopant gases, such as arsine, phosphine, and diborane, to be introduced into the deposition chamber. [539] The concentration of the dopant in the deposited film is controlled by the amount of dopant gas that is incorporated during the process. In addition to intentional dopants, autodoping can occur, which is the result of unintentional dopants being introduced from the substrate. [540] Therefore, minimum layer thickness requirements are often needed in order to compensate for autodoping.

Overall, epitaxial deposition methods allow for high growth rates of material, which allows films of considerable thickness (>100 µm) to form. They also allow for structured crystalline films of high purity and order, which allows for the production of high-performance devices. However, issues exist regarding epitaxial deposition methods in general, especially with manufacturing. [539] For example, outside of MBE techniques, it is sometimes difficult to control the composition and thickness of the thin film. It can be difficult to clean the deposition chamber, which in turn makes it difficult to maintain a desired level of purity in the film. The deposition surfaces need to be carefully protected during manufacture and handling. Depending on the

specific epitaxy process of interest, high substrate temperatures might be needed, which eliminates a large number of substrates for FHE applications.

A large amount of research involving epitaxial methods for FHE applications focuses on using graphene as the substrate material. In 2012, Norwegian University of Science and Technology (NTNU) published a paper describing their ability to grow vertically aligned GaAs NWs on atomically thin graphene using MBE. [543] The NWs were found to have a regular hexagonal cross-sectional shape due to the underlying graphene structure, and were all uniform in length and diameter. Their paper also presented a generic atomic model that demonstrated this process is applicable to all conventional electronic materials. They anticipate that their results will be applicable for optoelectronic applications and flexible, low cost solar cells.

NTNU has continued to work in this area and published another paper in April 2014, this time with the help of the IBM Zurich Research Laboratory. [544] In this work, they discovered that they were able to precisely control how the crystalline structure of the NW changes as it grows, and this control allowed them to create a structure that would be able to switch back and forth, with the help of a small electric current, between functioning as a LED and as a photodetector. Once again, they were using MBE to grow and control the structures.

This work, in addition to much more from the Department of Electronics and Telecommunications at NTNU, was spun-off in June 2012 into Crayonano AS. [545] Headquartered in Norway with a location in Palo Alto, California, Crayonano's goal is to continue to develop and commercialize the new hybrid electronics technology from NTNU. Currently their technology centers on the vertically aligned GaAs NWs grown on graphene by MBE, but they plan to start growing GaN NWs that can be used in white LEDs to result in better optical properties. [544] Crayonano's main application areas are flexible, transparent electrodes for solar cells and LEDs, but they are looking for industrial partners for further development of PVs, LEDs, thermoelectrics, piezoelectrics, and 3D ICs.

More information on the epitaxial growth of semiconductor NWs on graphene substrates can be found in a review put together by two researchers from NTNU in August 2013. [546]

Epitaxial growth can also be used with substrates other than graphene for flexible electronics purposes. For example, in July 2014, researchers from Friedrich-Alexander-University Erlangen-Nurnberg in Germany, published a report on the epitaxial growth of PbSe quantum dots on MoS2 nanosheets. [547] Hybrid structures were then created on PET substrates that were air-stable, solution processable at low temperatures, had good stability upon repeated bending, and were therefore applicable for low-cost flexible near-IR (NIR) photodetectors.

Additionally, a paper was published in September 2014 by a team from Seoul National University, Sejong University, and Kyung Hee University (all located in South Korea) that described another use of epitaxy for flexible electronics applications. [548] They used a van der Waals epitaxy process to deposit zinc oxide nanostructures on hexagonal boron nitride insulating layers. They then demonstrated an UV photoconductor device using the epitaxial-grown structure as an example of a device that could be made from this technology. They anticipate that

their work will enable the use of flexible and transferable inorganic electronic and optoelectronic devices in other applications as well.

While several examples can be found in academic literature that use epitaxial growth methods for FHE, commercial systems still seem to be targeted mainly for use with conventional rigid electronics and wafer processing. In fact, because epitaxy is widely used for electronics fabrication, several companies exist that use epitaxy methods or produce epitaxy systems and equipment. Some of these companies include LPE (Italy), Jenoptik (Germany), Veeco (Plainview, NY), Translucent, Inc. (Palo Alto, CA), Vinci Technologies (France), and IntelliEPI (Richardson, TX). Companies exist that are using epitaxial techniques for nanotechnology, but outside of Crayonano described above, no other companies were identified that target epitaxy specifically for FHE applications.

Because of its ability to create highly structured thin films of high purity and performance, it is no surprise that epitaxial growth methods are used often for electronics fabrication and wafer processing. However, since FHE are currently targeting lower-performing applications, epitaxy does not currently have as big of a role in this area, especially since it sometimes requires the use of high temperature environments. However, as academic institutions, such as the ones described above, continue to research the possibilities for epitaxy in FHE, and as companies such as Crayonano are spun off from these research efforts, epitaxial growth methods may become more prevalent in the FHE market.

4.1.2.2.10 Plating

Plating, also known as electrodeposition or ECD, is used to create thin layers of conductive material, such as copper, gold, or nickel, on a substrate. [449] Two main plating methods exist: electroplating and electroless plating. In electroplating, a substrate is placed in a liquid electrolyte solution, and an electrical potential is applied between a conducting area on the substrate and a counter electrode that is located in the solution. The result is the formation of a layer of material on the substrate through a chemical process. Gas is typically generated at the counter electrode as a byproduct. Electroless plating is similar to electroplating, just without the use of an external electrical current. In this process, a more complex chemical solution is used that allows for deposition to occur spontaneously on any surface which forms a sufficiently high electrochemical potential in the solution. The differences between the two processes are visually depicted in Figure 25.

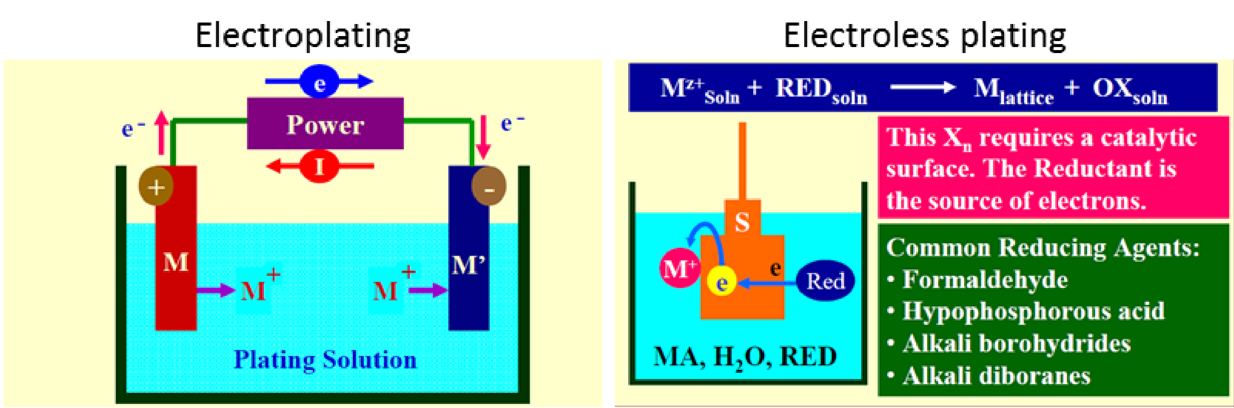


Figure 25. Electroplating versus Electroless Plating Technology [549]

Due to the spontaneous chemical reaction in electroless plating, an external electrical potential is not required and contact with the substrate during processing is not necessary, both of which offer electroless plating an advantage over electroplating in terms of cost and safety. [449] Electroless plating can also coat very diverse shapes and surface types. [550] However, the film thickness and composition is not as uniform with electroless plating as compared to electroplating. [449] Electroless plating is also slower and the deposited layers tend to be thinner. [550] Additionally, electroplating solutions are more stable than electroless plating solutions. No matter what process is used, the substrate must have an electrically conducting coating before the deposition can take place. [449]

Electrodeposition in general offers significant cost, reliability, and environmental advantages over various other deposition techniques. [551] The thickness of films created through electrodeposition processes can range from approximately one micron to greater than 100 microns. [449] One disadvantage of plating processes is the need for clean environments, since contaminants in the solution or on the substrates surfaces can cause the reactions to not take place properly. [550] Therefore, components are often pretreated with chemical in order to remove oils and other contaminants before deposition. [552] Another disadvantage of electrodeposition processes is the difficulty associated with coating parts with complex geometry. [3] While electroplating can typically produce more uniform layers than electroless plating, both processes tend to have large build-up on the outer edges of channels and crevices within parts.

Electrodeposition has various uses, including decoration (improving the appearance of jewelry, furniture, etc.), protection (wear and corrosion resistant coatings), electroforming (manufacture of parts), and enhancement (improve conductivity, solderability, reflectivity, etc.). [554] Perhaps of most interest to electronics is protection and enhancement. Plating can used to strengthen and increase the life of a component – for example, chromium plating helps to increase corrosion resistance. [4] Two very common application areas for electrodeposition are microelectronics and nanobio systems. [551] For example, in microelectronics, electrodeposition can be used in electronics processing to deposit flip-chip solder connects and copper interconnects, while in nanobio systems, it has been looked at as a way to deposit proteins.

The applications for which electrodeposition is used for traditional electronics can be carried over to FHE technologies, such as interconnects. For example, plating can be used to create copper foils that will be used as interconnects or conductive layers for flexible circuits. [555] But in addition to these, electrodeposition processes can be used for energy storage, solar cells, RFID tags, and medical devices, among others.

In 2011, researchers in Taiwan published an article detailing their work to create highly flexible supercapacitors. [556] In their work, they synthesized manganese oxide nanosheets on flexible carbon cloth using an electrodeposition technique. Their supercapacitors demonstrated excellent capacitance properties and high crack resistance, which they feel is highly promising for future applications in flexible energy storage devices.

Around the same time, researchers from South Korea and China published a report describing their work to create metallic NW-graphene hybrid nanostructures that can be used in the

fabrication of flexible field emission devices. [557] In this report, they describe how gold NWs were grown on the graphene surface through an electrodeposition method. The hybrid nanostructure was used as the cathode, and the entire structure exhibited stable and high field emission currents even when subjected to mechanical stresses. They also identify that these hybrid nanostructures can also be used as bio-chemical sensors, pressure sensors, and battery electrodes.

A report was published in 2013 describing how electrodeposition techniques could be used for solar cell applications. [558] A team from India and Japan successfully prepared nanocrystalline titanium dioxide thin film using an alkaline aqueous solution and a simple electrodeposition method. These electrodeposited films were then modified to create dye solar cells that had an overall light-to-electricity conversion efficiency of 2.1% under 1 sun illumination. This performance demonstrates that this electrodeposited film technology has high potential for consideration as a photoelectrode material for dye-sensitized solar cells (DSSC).

In addition to oxides, metallic NWs, and graphene, conductive polymers have also shown promise as a material that can be deposited through plating techniques. Conductive polymers have shown promise in many different flexible electronics applications, but their use is still limited by their processability. Researchers at The Hebrew University of Jerusalem in Israel published an article in 2013 describing their approach to overcoming this processability issue. [559] Using the previously known fact that silica can improve the mechanical strength and adhesion of conductive polymer films, they successfully created conductive polymer-silica hybrid thin films with an electrodeposition technique that could be used in flexible electronics applications. Through their work, they were able to optimize the deposition process and determine how film thickness and composition could be manipulated through process variables.

All of the examples mentioned above discuss using electrodeposition methods in general, but examples also exist that use specifically electroplating and electroless plating for FHE applications. A patent application filed in March 2012 by Second Sight Medical Products, Inc., based in California, describes a method of bonding a hermetically sealed electronics package to an electrode or flexible circuit for use as an implantation in living tissue, specifically for a retinal or cortical electrode array to enable restoration of sight to non-sighted individuals. [560] During the described method, electroplating a biocompatible material (platinum or gold) bonds the flexible circuit to the electronics package. Essentially, the electroplating process is used to package the medical device and ensure that it continues to have mechanical flexibility and functionality while in the body.

A patent application filed in October 2006 by Georgia Tech Research Corporation describes using electroless plating for FHE. [561] In their patent, they describe an RFID tag created on a flexible conformal substrate. The antenna is comprised of a thin-film conducting metallic material that is deposited by electroless plating onto the flexible PET substrate. They mention that electroless plating processes are relatively low-cost and low-temperature, and therefore they are ideal for commercial RFID production.

Several companies exist that perform electrodeposition techniques and/or manufacture electrodeposition equipment for a wide variety of industries, including electronics. A few of

these companies include Incertec (Fridley, MN), B&B Electroplating Co., Inc. (Linden, NJ), Sharretts Plating Company (Emigsville, PA), and Electronic Plating Co. (Cicero, IL). Like many of the other deposition companies mentioned, a large majority of these are not strictly targeting the FHE industry, but as can be seen above, plenty of examples exist that demonstrate the presence of this deposition method in the flexible electronics industry.

Because electrodeposition techniques are used heavily in the conventional electronics industry, it is not surprising that they are starting to catch on in the FHE world as well. Plating deposition is an inexpensive and easy method for depositing metallic and other conductive materials. Since a large impetus for FHE is ease of manufacture and cost, electrodeposition should be an enticing technology, especially for the lower performing electronics that are initially being targeted in the flexible hybrid market. Researchers are working to optimize the ECD process for materials typically associated with flexible electronics, such as graphene and conductive polymers. As further research is conducted, the market may see plating techniques used more often for flexible electronics in commercial applications.

4.1.2.3 Coating Methods

In addition to printing and deposition methods, coating techniques can also be used for the fabrication of FHE. Most coating techniques are roll-to-roll compatible and are used to cover large areas. Coating methods are typically inexpensive compared to deposition methods, and can usually be performed at or near room temperature, making them extremely desirable for FHE applications. While some basic patterning can be achieved, patterning while coating is generally not as easy as it is with printing methods. Overall, these methods are often simpler and easier to use than other printing or deposition methods, and therefore are often used in laboratory and R&D environments where FHE applications are being developed.

This section is comprised of analyses of several different coating methods, including spray coating, slot die coating, spin coating, and knife coating/doctor blading. Each analysis includes a general summary of the technology, followed by examples of the coating methods being used in FHE applications. Additionally, various companies are provided for each technique that either perform coating services or produce coating equipment.

Table 18 provides a snapshot summary of the information described in the following coating sections. The categories across the top of the table are the main topics of interest when discussing a particular coating method. The color-coded boxes give insight into how each method performs with respect to each category. A green box indicates that the coating method performs well for that category, while a red box indicates that particular area is not a strong suit of the coating method. Yellow boxes indicate that the coating method does not excel nor lag behind in that particular area.

Table 18. Summary of Characteristics of Coating Methods for FHE

	Control Over Film Thickness/ Composition / Purity	Cost	Patterning Capabilities	Material Usage (no waste)	Roll-to-Roll / Large Area Compatible
Spray Coating					
Slot Die Coating					
Spin Coating					
Knife Coating					

4.1.2.3.1. Spray Coating

Spray coating is a well-established coating method for graphic arts, industrial coatings, and painting. [562] Slightly less complicated than several of the other deposition methods mentioned previously, spray coating involves forcing a material through a nozzle to form a fine aerosol, which is then directed at a surface through various methods, including the use of carrier gas or electrostatic charging. [563] The aerosol then deposits on the substrate to create a thin film, as shown in Figure 26.

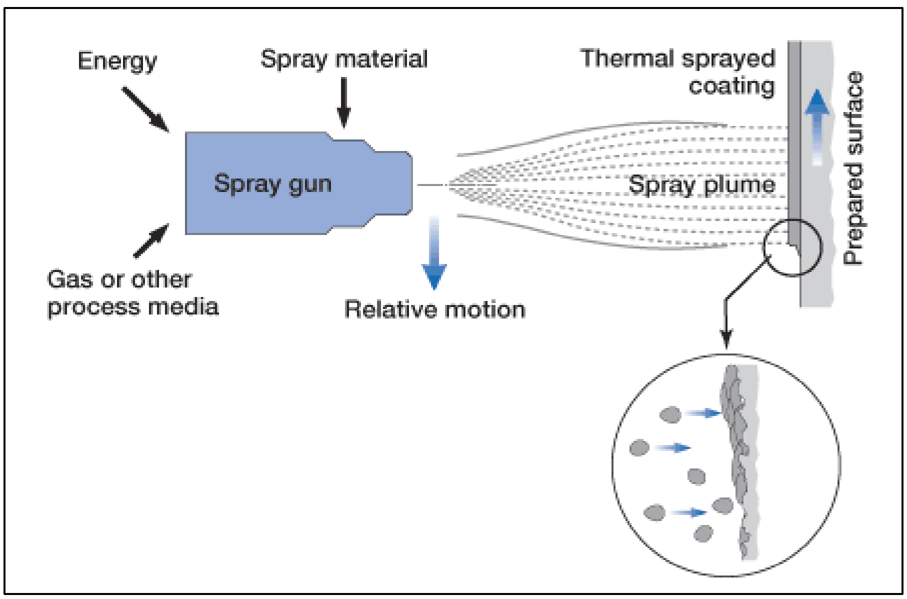


Figure 26. Spray Coating Technique [564]

Spray coating is a high-throughput large-area deposition technique that is often used for in-line production and roll-to-roll applications. [562] Spray coating can apply a wide variety of materials with different rheology and viscosities, and the coating systems can be tuned and optimized for the specific material of interest. Coatings can be applied in a wide range of thicknesses to a large number of surfaces, including substrates with unique and complex surface morphologies. Similar to most of the other deposition methods mentioned above, this type of coating can be performed without physical contact between the coating head and the substrate. [565]

Despite these benefits of spray coating, it can be difficult to control the thickness and roughness of the deposited film, which makes high performance devices less attainable. [562] Additionally, while shadow masks can be used to pattern the coating, more development will have to be performed in order to achieve high control over the pattern. [565] Automated and computer controlled spray coaters are being investigated to address this issue. [562]

Spray coating techniques have been increasingly used for FHE applications, specifically for organic materials and CNTs. A patent application was filed in December 2004 by Eikos, Inc. describing a polymer binder that can be used with CNT-based flexible, transparent conductive coatings. [566] In the text of their patent, they describe that the binder and the CNTs can be applied by any traditional coating process, which includes spray coating, among others. In their supporting examples, they use spray coating almost exclusively to apply the CNTs to the flexible substrate.

In 2009, an article was published by researchers from Belgium that describes their work exploring spray coating as a deposition technique to fabricate solution-processed polymer solar cells based on organic semiconductors. [562] They focused their studies on the influence of the airbrush settings on the film topography and how that quality corresponded to PV performance, but overall they were able to prove that spray coating is a viable technique for the fabrication of organic solar cells and an excellent alternative to other commonly used methods.

Another article in 2009 from researchers at Dresden University of Technology and Fraunhofer Institute in Germany describes using a spray coating process to create SWCNT thin film electrodes. [567] The electrodes were intended for use in alternating current electroluminescence (ACEL) devices. The spray coating process allowed the team to have control over the transparency and sheet resistance, which resulted in emission intensities that were as high as that for ITO-based ACEL devices.

In 2013, a team from Technische Universität München in Germany researched how spray coating compared to transfer printing, with an ultimate goal to deposit high quality CNT films on flexible substrates. [568] Their first method, transfer printing, involved printing CNT films on glass and then transferring the films to the flexible substrate. The second method involved spray coating the CNTs directly onto the flexible substrates. Both processes were reliable, reproducible, and resulted in highly uniform CNT films that were comparable to state-of-the-art CNT films that were fabricated and remained on glass substrates. The spray coating method had an advantage however because it eliminated the transfer step.

Because spray coating is such a widely used technique, especially in the graphic arts, industrial coating, and painting industries, countless companies exist that perform spray coating or sell spray coating equipment. Several of them are even targeted for conventional electronics applications. These companies, which include ASB Industries, Inc. (Barberton, OH), Magic Spray (Santa Clara, CA), and RiverBend Electronics (Rushford, MN), apply electrically conductive coatings, dielectric coatings, electromagnetic interference (EMI) shielding coatings, and corrosion and wear resistant coatings, just to name a few. A couple companies exist that are also beginning to target FHE, and Sono-Tek Corporation in Milton, NY, is one of them. [569] Sono-Tek designs, manufactures, and services precision ultrasonic spray coating systems for

several industries, including electronics, energy, medical, glass, food, textiles, and nanotechnology. Within their electronics expertise, they provide systems that can be targeted for CNTs, graphene, NW, and TCO deposition, as well as for OLED production.

While spin coating, which is discussed in Section 4.1.2.3.3, is considered more reliable and reproducible than spray coating, recent developments in spray coating technology have allowed it to catch up to spin coating, and it offers the additional benefit of being compatible with roll-to-roll production lines, an extremely desirable trait for FHE applications. [562] Recent work has also demonstrated that spray coating has considerable promise as a scalable technique for large area devices, especially since it requires relatively simple equipment. Because of the fast drying times characteristic of this process, possibilities exist to create more complex flexible devices using multi-pass lines. Therefore, it is not surprising that spray coating is already being used for the FHE applications mentioned above, and it is expected that it will be used even more often in the future as roll-to-roll production of electronics becomes more prevalent.

4.1.2.3.2 Slot Die Coating

Slot die coating, demonstrated in Figure 27, is a non-contact large-area coating method used to create homogeneous thin films with high cross-directional uniformity on a variety of substrates, including glass, stainless steel, and plastic. [570, 571] This type of coating system is considered pre-metered, which means that all of the liquid supplied to the die head is directly transferred to the web, with no material wasted in the process. [572] The nozzle is also completely enclosed within the coating system, which allows for an extremely clean process and reduced contamination opportunities. The coating process in itself is quite robust and straightforward, as the head is easily aligned and simply translated perpendicular to the direction of the web movement. [563] The coating technique is roll-to-roll production compatible, and is capable of achieving high production speeds. [573]

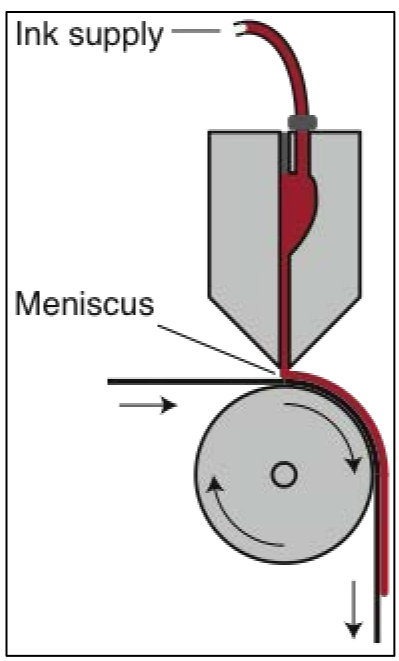


Figure 27. Slot Die Coating Schematic [570]

Having a pre-metered process allows for control over flow rate and film thickness. [570] The coating thickness can be controlled by the web speed, coating width, and the flow rate of the liquid to the die head. [572] With this process, it is possible to create very smooth and uniform coatings that range from approximately 2 – 400 microns. The systems can also handle various viscosities.

Despite the many advantages, there are a few drawbacks to the slot die coating process. The coating head can be quite complex compared to other coating systems, but a significant amount of research has been and continues to be performed on slot die coating process in general and regarding the coating die head specifically. [563] During the coating process, the die lip is extremely close to the substrate, which can lead to damage to both the lip and the substrate. [574] Additionally, while having an enclosed system helps to reduce contamination opportunities, the system is still very sensitive to dirt sediments and air bubbles, and if contamination does occur, a large amount of effort is required for cleaning.

Slot die coating is becoming an essential tool in the optical coating and PVs industries, but it can also be used for multilayer ceramic capacitors, lithium ion rechargeable battery electrodes, polyimide (PI) coatings for flexible printed circuits (FPCs), inkjet photo paper coatings, film casting, automotive rubber sheet casting, and nanomedicine applications. [572] Specifically in the PV industry, slot die coating has been used to apply zinc oxide, active layers, PEDOT:PSS, and even silver to create both organic and inorganic solar cells.

As already mentioned, slot die coating is used prevalently in the FHE market, specifically in PVs, lighting, and electrodes. In 2009, a researcher from the Technical University of Denmark published a paper describing how slot die coating, in addition to knife-over-edge coating and screen printing, could be used to prepare polymer solar cell modules in a roll-to-roll fashion. [575] Since then, countless papers have been published that have worked to optimize the slot die coating process for solar cell applications and make it applicable for several different chemistries. [576, 577, 578, 579]

Outside of solar cell technology, slot die coating can also be used to produce flexible electrodes for various applications. In 2014, researchers from the Jawaharlal Nehru Center for Advanced Scientific Research in India and the Technical University of Denmark published a report that documented their work in slot die coating for flexible electronics. [580] They described how slot die coating could be used as a simple method for producing patterned silver electrodes on transparent and flexible substrates. Through this process, the electrodes exhibited excellent adhesion and mechanical properties, which is important for implementation into flexible electronic devices. They were able to demonstrate low voltage heaters, pixelated electrochromic displays, and organic solar cells using their slot-die manufactured electrodes.

Slot die technology can be used for light emitting applications as well. A paper published in 2012 describes the work performed by a team from Umeå University in Sweden and the Technical University of Denmark on fabrication of flexible electronic devices using slot die methods. They describe the completely solution-based fabrication of an alternative emissive device, a light-emitting electrochemical cell, using a slot die roll-to-roll apparatus. The entire

fabrication process was performed under ambient air conditions, which could lead to significant cost savings.

Slot die coating is highly prevalent in the commercial market, and in fact, many companies exist that target slot die coating for flexible electronics applications. At the 2015 Flexible and Printed Electronics Conference hosted in Monterey, California in February 2015, several slot die coating companies, including Frontier Industrial (Towanda, PA) and nTact (Dallas, TX), were in attendance and even exhibiting some of their products, which is a clear indication of the presence of slot die coating within the flexible electronics industry.

Frontier Industrial manufactures slot die equipment for both roll-to-roll and sheet fed systems. [581] Their product line includes full production scale systems, pilot scale systems, demonstration coaters, glass and sheet coaters, micro-control coaters, and compact slot die laboratory coaters. They also have an R&D/pilot lab where their customers can test their own formulations and designs on Frontier's equipment. In fact, Frontier Industrial is currently working with Corning to determine if Willow® Glass is compatible with their slot die roll-to-roll coating systems. (A description of Corning's Willow® Glass can be found in Section 3.4.4.) Currently, their technology can handle a very wide range of viscosities and formulation compositions, and to date, the largest equipment they have produced can handle films up to 100 inches wide. Applications of interest for their equipment include electronics, microcircuit materials, and LCD and OLED display components.

NTact designs, develops, and manufactures advanced, high precision slot die coating systems for the display, microelectronics, alternative energy, and thin film industries. [582] They feature systems for both lab and full production scale environments, and they can be fully integrated, roll-to-roll compatible, and can even include web cleaning and pretreatment functions. NTact's slot die systems can be used for flat panel displays (LCD, OLED, flexible), PV panels, solid state lighting, and various other organic and printed electronic applications such as RFID, polymer batteries, sensors, and others.

MBraun, a German company with a U.S. location in New Hampshire, is a market leader in providing customer-specific controlled environment solutions, particularly in gloveboxes, inert gas purification, thin-film technology, isolators, and custom clean environment system solutions. [583] In March 2013, a press released announced that MBraun would be teaming up with nTact to offer a complete slot die coating system solution that features nTact coaters with MBraun gloveboxes. [584] These combined systems allow for the high quality inert coating systems that are available for all stages of development, from research to full-scale production. Through these systems, both companies hope to better serve the OLED, display, solid state lighting, and PV industries. Through this collaboration, MBraun is able to offer systems that coat both organic and inorganic materials on flexible and rigid substrates and are capable of coating thicknesses that range from 20 nm to approximately 150 microns.

As demonstrated, slot die coating is already being heavily used for FHE applications within both academia and industry. With all of the advantages that slot die coating offers, including control over thickness and uniformity, ability to produce little-to-no waste, closed systems that minimize contaminants and messy cleanup, and the compatibility with roll-to-roll production, it is not

surprising that this low-cost system has become so popular. As long as complex patterning is not required for at least a portion of the electronics fabrication, slot die coating will most likely continue to be a go-to coating method for FHE applications.

4.1.2.3.3 Spin Coating

Spin coating is a well-known method for depositing relatively uniform films on flat substrates [585]. This type of coating technology is used to deposit materials in a variety of applications, including photoresist and dielectric for microcircuit and semiconductor fabrication, OPVs, magnetic disk coatings, antireflection coatings for flat screen displays, coatings for compact disks, and television tube phosphor and antireflection coatings. [586]

The spin coating process is typically broken down into four key stages, which are depicted in Figure 28. First, the substrate is mounted onto a rotating device, and the liquid coating material is dispensed onto the substrate, either by hand or with an automated nozzle/sprayer. [587] The coater then begins to spin, and the substrate is accelerated up to the desired speed. [586] During this stage, the rotational motion leads to significant fluid expulsion from the substrate surface, but it also helps to spread out the coating material. In the third stage, the coater reaches a constant spinning rate, and fluid viscous forces dominate fluid thinning and coating behavior. [586] The fluid thinning is typically consistent, creating a relatively uniform coating, except for at the edges of the substrate, which normally have a buildup of droplets. The last stage of the spin coating process is when the substrate is spinning at a constant rate, but solvent evaporation dominates the thinning behavior. During this stage, the fluid flow due to viscous forces becomes almost negligible, and evaporation of any volatile species in the coating material becomes the dominant process. This process can also be assisted through the use of heat treatments. It is important to note that stages three and four occur simultaneously, but viscous effects dominate at the beginning of the spin coating process while evaporation takes over towards the end of the process.

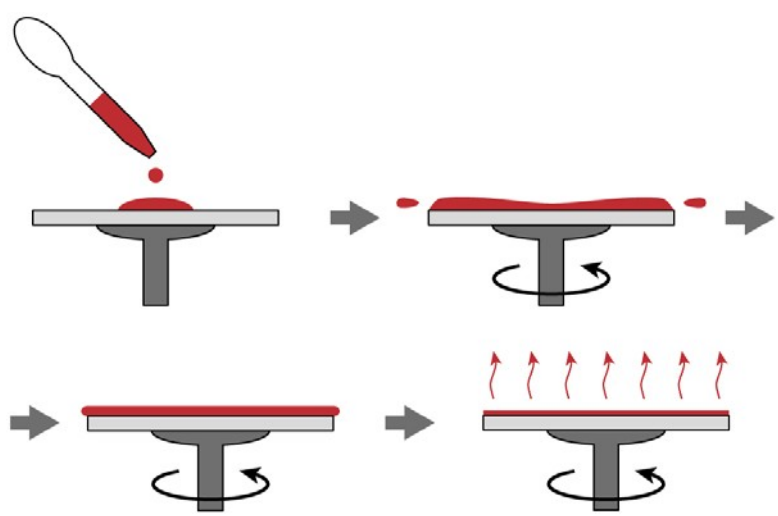


Figure 28. Spin Coating Flow Diagram [587]

The thickness and uniformity of the deposited coatings are primarily dictated by the viscosity of the coating material and the spin speed. [588] For thicker films, high viscosity materials, low

spin speeds, and short spin times are necessary. Coating thicknesses achieved through spin coating techniques typically range from less than 10 nm to 200 µm, but coatings thicker than 15 µm usually require multiple rounds of coating.

Spin coating is a simple, inexpensive coating technique, and its process variables are easy to manipulate. [589] Spin coating can also create coatings of uniform thickness on a variety of substrates. [587] Spin coating is a very quick process that can be used with a multitude of materials, making it an efficient screening tool. [590]

However, spin coating is difficult to scale to large area samples, and since it is a batch process, it has a relatively low throughput compared to roll-to-roll technologies. [587, 587] Unfortunately, material usage is typically around 10% or less, with the rest being flung off the substrate and wasted. Furthermore, the consistency of the film thickness from one sample to another can be difficult to control, especially if the coating material is applied before spinning. The time elapsed between material being placed on the substrate and the start of spinning heavily affects the film thickness and quality. [591] Therefore, instead of depositing the coating material onto the substrate before it starts spinning, the coating material can alternately be dispensed onto the substrate after it has already reached the desired speed. In this case, the solvent has less time to evaporate, which can sometimes lead to a more controlled process with more uniform coatings and less variation from sample to sample. However, at low spin speeds, depositing the material in this manner can lead to incomplete substrate coverage. As a result, the method used should be chosen depending on the spin speeds and the intended application.

As previously mentioned, spin coating has been used for a while in traditional electronics manufacturing, but it is becoming extremely popular for FHE as well. Spin coating is often referred to as one of the most commonly used thin film fabrication techniques for organic electronics, and because it is a simple and inexpensive technique, it is often found in laboratories that are researching FHE. [592] Many examples can be identified within the last ten years where spin coating was used to create electrodes, transparent conductors, and semiconducting films.

In 2004, researchers from IBM T. J. Watson Research Center in New York published a paper detailing how high-mobility ultrathin semiconducting films were prepared by spin coating techniques. [593] They were looking for thin-film semiconductors that could simultaneously provide high carrier mobility, convenient solution-based deposition, and low cost fabrication for use in applications such as flexible and wearable computers, large area displays, and electronic paper. In their work, they created continuous crystalline metal chalcogenide films that were used to fabricate thin-film field-effect transistors. Through their experimentation, they believed their spin coating method could be applicable to a range of metal chalcogenides to fabricate several different thin-film devices, including solar cells, thermoelectrics, and memory devices.

While spin coating can be used to deposit semiconducting films as seen in the example above, more recently it has been widely used to create various types of electrodes for flexible electronics applications. A team from University of California at Los Angeles (UCLA), published a report in 2009 documenting their work to create high-performance transparent conductors from both graphene and CNT materials. [5] They used spin coating to create a nanocomposite comprised of chemically converted graphene and CNTs. By using spin coating

techniques, they were not required to use surfactants, which preserved the intrinsic electronic and mechanical properties of both the graphene and CNT materials. They believe that their spin-coated nanocomposite material could be used as a transparent electrode for flexible electronics applications.

A team from Korea published the work they performed to create transparent electrodes using spin coating methods. [595] They recognized the increasing prevalence of FHE and sought to find a replacement for ITO in transparent electrodes. They focused their research on silver NWs, and were able to create flexible transparent electrodes with superior mechanical, electrical, and optical properties by embedding a silver NW film into a transparent polymer matrix. Through the use of their spin coating method, they produced electrodes that are ultrasmooth and deformable, and also have sheet resistance and transmittance comparable to ITO electrodes.

Another example of spin coated electrodes demonstrates that coating and deposition processes can be combined to create a final product. A research team from Jilin University in China, also mentioned in the ALD Section 4.1.2.2.2, used spin coating techniques to create silver NW meshes, and then used low-temperature ALD to fill in the voids in the silver NW mesh with zinc oxide. [468] This combined process allowed for efficient charge extraction/injection in the flexible electrode product.

In addition to silver NW-based electrodes, spin coating techniques can also be used to create polymer-metal hybrid electrodes for flexible electronics. Researchers from the Gwangju Institute of Science and Technology in Korea published an article in 2015 detailing their work to create flexible and transparent electrodes. [503] (Their report was also mentioned above for the vacuum evaporation techniques they used to deposit the conducting silver layers.) This team used spin coating to deposit the various polymer layers needed to create the electrode. Their final product is able to function as a universal electrode for high-end flexible electronic applications, such as polymer solar cells with a power conversion efficiency near 10% and polymer LEDs that can outperform those based on transparent conducting oxides.

Because spin coating is such a widely used technique for a variety of industries, numerous companies exist that either perform spin coating or produce spin coating equipment, and a few of these companies are specifically focused on electronics. Ossila, located in the United Kingdom, was founded in 2009 by organic electronics research scientists with the aim of providing the components, equipment, and materials to enable faster and smarter research and discovery. As part of their equipment line, they have a spin coater designed for laboratory environments that functions without vacuum in order to help reduce substrate warping, improve film uniformity, and decrease costs. MBraun, mentioned above as a provider of slot die coating equipment, also has a line of spin coating technology ideal for R&D environments and pilot scale manufacturing. Specialty Coating Systems, Inc., located in Indiana, offers various types of coating and manufacturing equipment, including spray coating and dispense systems, curing systems, dip coating systems, ionic contamination test systems, parylene deposition systems, and spin coating systems. Brewer Science, a company located in Missouri which also makes CNT inks for flexible electronics applications, produces spin coating equipment designed for R&D and other small scale operations. Along with these highlighted companies, Headway Research (Texas), Solitec Wafer Processing, Inc. (California), Bid Service (New Jersey), Laurell (Pennsylvania),

Chemat Technologies (California), and Ultra T Equipment Co. (California) all produce and/or sell spin coating equipment.

While spin coating has many advantages, including simplicity, cost, and versatility, there are unfortunately important aspects about this technology that might keep it from being widely used as FHE transition from R&D to a widely used and produced technology. First of all, a significant amount of ink is wasted as part of the spin coating process, which is extremely disadvantageous when some FHE inks use expensive metals like silver. As can be seen with the companies mentioned above, spin coaters are mainly designed for laboratory or small scale production environments, and they are certainly not yet compatible with roll-to-roll manufacturing.

Since spin coating systems are used heavily in electronics and wafer manufacturing, they are typically used with hard and rigid substrates. While some efforts have been made to attempt to make spin coating systems compatible with thin and flexible substrates, not all spin coatings systems can support the new innovations. Brewer Science developed a porous ceramic insert design that supports a substrate, rigid or flexible, by distributing a vacuum evenly across the backside of the entire substrate. [596] Brewer Science also has similar technology that allows for non-circular substrates to be used. Unfortunately, many standard spin coaters lack the necessary horsepower in their drives to use both of these technologies.

Therefore, while spin coating will most likely continue to be used heavily in laboratory environments for both conventional and FHE applications because of its simplicity and inexpensive nature, it is doubtful that this coating method will be a leading technology for large scale manufacturing of FHE anytime in the near future.

4.1.2.3.4 Knife Coating/Doctor Blading

Knife coating or doctor blading is a type of coating technique used to create large area films on flexible or rigid substrates. [597] The process involves placing the ink in front of a blade and then moving the blade across the substrate surface (or moving the substrate against the fixed blade). This coating method, shown below in Figure 29, can be used in both batch and roll-to-roll systems. [563] In batch systems, the method is called doctor blading, and the blade is pulled across the flat substrate to distribute the ink. When doctor blading is made roll-to-roll compatible, it is referred to as knife coating or knife-over-plate coating, and the blade is held fixed as a substrate on a roller is brought past the blade. In the rest of this discussion, the terms knife coating and doctor blading will be used synonymously.

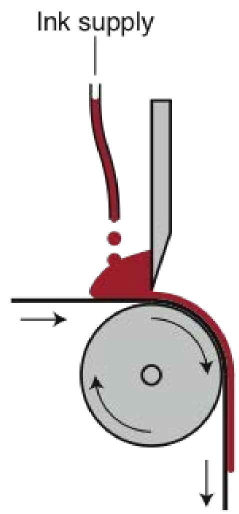


Figure 29. Doctor Blade Coating Technique [597]

The thickness of the coating is controlled by the size of the gap between the blade and the substrate surface. The final wet thickness of the film is ideally half the gap width, but this depends on the surface energy of the substrate, the surface tension of the fluid, coating speed, viscosity, and surface temperatures, among other factors. [563]

Knife coating/doctor blading is a relatively simple and inexpensive coating method. However, patterning during knife coating is almost impossible, and film formation/drying in doctor blading is relatively slow, which could lead to issues if the material has a tendency to aggregate or crystalize. [563] Knife coating is often compared to spin coating, and is used for many of the same application areas. Like spin coating, it is often used in laboratory environments due to its simplicity and cost. [597] However, unlike spin coating where a significant amount of ink is wasted, almost all of the ink in a knife coating process is applied to the substrate. Additionally, knife coating can be used in a roll-to-roll manufacturing environment, where spin coating cannot. One of the most prominent applications for knife coating in FHE is for solar cells. Countless examples can be found in literature demonstrating the use of doctor blading for solar cells fabrication, particularly for polymer solar cells. In 2006, researchers from Konarka Technologies in Austria published a paper describing their method of printing bulk heterojunction solar cells from poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) using a doctor blading method, which could achieve efficiencies over 4% [598]. Two years later, a nuclear magnetic resonance (NMR) study was conducted in Belgium on thin films of polymer blends used in organic PV devices, and the thin films were created using both spin coating and doctor blading. [599] In 2011, a report was published detailing work performed at the Karlsruhe Institute of Technology in Germany using knife coating to create polymer nanoparticle films for hybrid polymer solar cells. [600] Many other examples of this same kind can be found throughout literature. [563, 565]

In addition to solar cell applications, doctor blading can be used for TFTs and electrodes, among other applications. A report published in Applied Physics Letters in 2013 describes how single-grain silicon TFTs can be created on flexible PI substrates through doctor blading liquid silicon. [601] Through a low temperature (350 °C) process, researchers were able to achieve a carrier mobility of 460 cm2/Vs and 121 cm2/Vs for electrons and holes, respectively. Though they were

fabricated on a PI substrate, the devices were able to be peeled off and transferred to PEN substrates to create flexible devices. In 2012, doctor blading was used to create a thin flexible polypyrrole-lithium iron phosphate-based cathode on an aluminum/carbon film substrate. [602]

While it is clear that doctor blading/knife coating is often used for the PV industry, among others, only a few examples of companies performing knife coating and/or producing knife coating equipment could be found. Yasui Seiki Co., a Japanese company, produces a piece of equipment called βCoater™, which is a small, adjustable, precision knife-over-plate coating machine for test coating on both rigid and flexible substrates. Yasui Seiki's sister company, Mirwec Film, located in Indiana, is the only authorized vendor in the U.S. for original Yasui Seiki coating systems. KKA, headquartered in Germany, has a line of Techtonys knife coating machines that feature floating doctor blade head capabilities. These systems are extremely flexible, can be adapted to a variety of production requirements, and can coat widths ranging from 500 – 5500 mm. Coatema Coating Machinery GmbH, also located in Germany, has laboratory, pilot, and production scale equipment that feature knife coating capabilities. Several companies also offer knife coating services, including Mirwec Film, mentioned above as a distributer of Yasui Seiki equipment, and Appvion, Inc., located in Wisconsin. Mirwec Film provides coating services to customers in various industries, including FHE, and Appvion has coating services for a variety of methods, including knife, blade, flexography, and gravure.

Companies also exist that simply produce the doctor blades used in these systems. These blades can be used on knife coating systems, or alternately can be used to allow a different system to have knife coating capabilities. Flexo Concepts, headquartered in Massachusetts, designs and manufactures doctor blades for narrow web, wide web, corrugated, and offset coating applications. In addition to blades, they also have roll cleaning technologies. Esterlam, located in England, also produces advanced doctor blade technology. Their technology, which they mention can be used specifically for electronics applications, can be successfully used on all major coating machine types, including systems from Kroenert (Germany) and Polytype America (New Jersey).

Even though film formation can be slow and patterning is not possible, knife coating has still found its place within the flexible PV industry due to its simplicity, cost, and roll-to-roll compatibility. Also, because of these factors, it is often found in laboratory environments as an R&D tool, similar to spin coating systems. While these two areas will most likely stay the dominant applications for knife coating in FHE for the foreseeable future, it is not unlikely that other applications will emerge, especially since this coating technology is roll-to-roll compatible, giving it an advantage over spin coating systems.

4.1.3 Post-Processing Methods

After inks are applied to the desired substrate, most of the time the system needs to go through various post-treatment processes in order to obtain full functionality. [603] A majority of the post-treatment processes that an ink can undergo could fall under the broad term of curing.

According to the ASM Materials Engineering Dictionary, to cure means "to change the physical properties of material (usually from a liquid to a solid) by chemical reaction or by the action of heat and catalysts, alone or in combination, with or without pressure". [604] There are various

curing methods used for inks, including thermal, photonic, UV, IR, chemical, and sintering, and each of these are discussed in detail below. In general, these methods alter the inks in three different ways: through removal of components, addition of components, or by causing changes to the components within the formulation.

4.1.3.1 Thermal Curing

Heat treatment refers to methods that use thermal energy to induce physical and/or chemical changes in a material. [605] For FHE, thermal curing can be used to remove and change components within the formulation. Thermal curing, and heat treating in general, is a widely used tool in a large number of manufacturing environments. Therefore, because of its prominence, simplicity, and low cost, it is by far the most popular curing method for FHE. However, there is a large push within the industry to find alternative techniques that will not harm the temperature sensitive materials and substrates that are being used for FHE. This section is focused on the thermal curing mechanisms used for FHE, but other non-thermal methods are thoroughly discussed in subsequent sections.

The majority of functional ink formulations include a liquid carrier in the form of an organic or aqueous solvent. [428] The liquid carrier is the medium by which the functional materials are deposited onto the desired substrate through a particular printing method. Once the functional materials are on the substrate, the liquid carrier no longer has a function and can be removed. Occasionally, this does not require any additional energy source if the liquid carrier is volatile at application temperatures. However, most often, thermal energy is used to evaporate the solvent. [606] Ideally, the solvent system should be designed so that it evaporates or decomposes at a relatively low temperature that does not damage the remaining components of the ink formulation or substrate. Other volatile components and/or additives in addition to the solvent could be removed through thermal curing as well.

As described previously, oftentimes nanomaterials in a printed electronics ink are surrounded by ligands that perform various functions. Metal complexes by design are metal particles surrounded by bound ligands, and the ligands dictate the reactivity of the central atom. [6] Ligands can surround a nanoparticle in order to protect it from oxidation and aggregation, and they can also cause the nanoparticle to have increased solubility in organic solvents. However, once the ink is deposited, these ligands form an insulating barrier and need to be removed in order to realize the full functionality of the nanoparticle. [607] Exposure to thermal curing allows the ligand-nanoparticle bonds to break and the ligands to be removed through evaporation or decomposition, which ideally happens at low temperatures. [606, 608]

Other than removing materials, thermal curing can also be used to simply cause changes to the materials within the composition, and these changes can then affect the overall functionality. Heat can activate a thermal initiator in the composition that causes crosslinking of a polymeric component, such as a binder or functional polymer. [609] For a polymeric binder resin, the crosslinking helps to lock materials in place and increase adhesion to the substrate. [610] Crosslinking the functional polymer dissolves boundaries between individual polymer chains, providing connectivity channels that allow the polymer to carry out its function. Thermal curing mechanisms would be applicable for any formulation that uses a binder or a functional polymer (conductive, semiconductive, dielectric). Similarly to how that thermal curing induces polymeric

materials to crosslink and fuse together, thermal curing can also be used to cause conductive particles in a formulation to fuse together through a method called sintering. This method will be described in more detail in Section 4.1.3.6.

Thermal curing is one of the simplest, most comprehensive, and most widely used methods of curing, but it does have some disadvantages. Thermal curing methods heat the entire product instead of just the ink formulation, which uses more energy than necessary. [611] Heating the entire product also causes problems if the substrate or any other component in the formulation is thermally sensitive. [428] Thermal curing can also be a time intensive process, requiring the products to be taken off-line to cure in an oven, disrupting the process flow. [611]

Most thermal curing for flexible electronics is simply performed in an industrial oven, and these types of ovens are produced by countless manufacturers all over the world. [612] Thermal processing equipment can be used interchangeably for many different manufacturing processes, and therefore not many companies produce thermal ovens strictly for the printed electronics industry. However, despite the wide availability of these ovens, some disadvantages also exist. Since thermal curing can take minutes to complete, these ovens need to be extremely large to compensate for fast line speeds that would be associated with roll-to-roll manufacturing, which uses up valuable production space. [611] An alternative to this option, as mentioned above, is to dry and/or thermally cure the products off line, but this disrupts the process flow.

Since the industry is trying to move away from thermal curing due to the desire to use temperature sensitive substrates, and because of the other disadvantages mentioned for thermal curing, not as much academic research is being conducted regarding thermal curing processes or thermal curing equipment. A majority of the investment regarding thermal curing processes instead involves researching materials that can be sintered at lower temperatures, which is discussed throughout the materials section of this report. The remainder of this section will discuss the alternative post-treatment process that are being researched as a replacement for thermal curing, including the various academic institutions and companies involved in the investigations.

4.1.3.2 Photonic Curing

Photonic curing, simply by understanding the two words that make up the phrase, would appear to encompass curing techniques carried out with the use of light. However, there seems to be some inconsistencies in the industry as to what exactly falls under the “photonic curing” umbrella. Some sources state that photonic curing can be achieved with either pulsed light or lasers. [613, 614] Others, including leaders in photonic curing for printed electronics, define photonic curing as a method that strictly uses pulsed light, not laser light, to process materials. [615, 616] Therefore, subsequent mention of photonic curing in this document will refer to pulsed light curing, and curing using lasers will be called laser curing.

Both pulsed light and laser curing can operate over a wide range of the electromagnetic spectrum, from UV through IR. However, there are specific curing techniques that use strictly UV or IR technology. While these technologies can technically be considered photonic curing as well, they will be discussed in their own separate sections below.

Photonic curing is a method using pulsed light from a flashlamp to process a thin film at high temperatures without damaging the substrate underneath. [617] During the process, a high power, short pulse of light heats the desired material, which can raise the temperature of the material above 1000° C. With this pulse, the substrate can increase to above its maximum working temperature, but the pulse occurs so quickly that there is not enough time for the properties of the substrate to be significantly changed. This process allows materials to be cured in less than a second, making it compatible with high speed printing. The wavelengths of the light pulse are between UV and IR, with the greatest intensity in the visible range. [618] Photonic curing can perform nearly all of the same functions as thermal curing, including sintering metals, drying films, and initiating chemical reactions, but it is not effective for use with organic inks. [619, 620] Photonic sintering will be described in more detail in Section 4.1.3.

Photonic curing was first developed by NovaCentrix and was introduced in 2006 at the Nano Science and Technology Institute (NSTI) conference. [615] Today, photonic curing technology has been incorporated into NovaCentrix's PulseForge tools, which are designed specifically for printed electronics applications. NovaCentrix also offers customized systems where the user can control both the intensity and the duration of the light pulses, a technique referred to as "digital sintering," and Chemnitz University of Technology in Germany is one of the universities that is using these digital sintering systems to investigate printed electronics. [621]

While NovaCentrix is the leader in photonic curing for printed electronics technology, a couple other companies also offer similar products. Xenon Corporation in Massachusetts has a Sinteron Series of photonic sintering tools for printed electronic inks, and a dual-stage pulsed light system for curing applications. [616] Additionally, Dresden Thin Film in Germany describes one of their product offerings as a "short time annealing process" where flash lamps are used to anneal materials or dry solvents. [622]

Various companies and universities are using photonic curing technology in their flexible electronics research. For example, researchers from Technische Universität Berlin in Germany published a paper in December 2014 detailing their work to create OFETs. [623] In their report, they describe how they used photonic curing methods to anneal layers of HfO_2 sol-gel dielectrics to achieve high-quality insulating layers for their field-effect transistors. Their photonic curing process could be carried out within a few seconds and led to the reduction of leakage current density of more than three orders of magnitude as compared to dielectric layers formed from highly sophisticated ALD. DuPont filed a patent application back in 2011 that utilized photonic curing methods as part of the described process. [624] The patent application was for a method of manufacturing glass coated flexible polymeric substrates that are suitable for flexible solar cells and other electronic devices. Their process involves applying a glass precursor layer onto a polymeric substrate and then photonically curing the system, resulting in a substrate that is flexible, roll-to-roll compatible, and has the surface properties of glass.

Since flash lamps have such a wide spectral emission, photonic curing is often considered for large-area printed electronics. [613] However, if the substrates are even partially absorbing, the wide emission can cause damage. Additionally, unprotected areas of the substrate can be exposed to the light pulse. Laser curing is an alternative that could help address this issue, since the process involves a focused beam of energy that targets a very specific area. Laser curing

functions very much in the same way as photonic curing, except with the light source being a laser instead of a flashlamp. Unfortunately, lasers are much more expensive light sources, and are not as practical or efficient when trying to treat a large area. [614]

The light sources used in light curing equipment (which includes photonic, laser, UV, IR, etc.) can be classified into three groups: spot, flood, and focused. [625] Spot cure systems focus high levels of light into small areas. Flood systems are used to target larger areas, but with lower levels of light energy. Focused systems, combining the beneficial aspects of these two systems, have the ability to irradiate large areas with high intensity light. The light source chosen depends on the specific needs for the particular application of interest.

4.1.3.3 UV Curing

UV curing is used mainly to physically and/or chemically alter the components within a formulation, as opposed to adding or removing components. Instead of heat, UV curing methods use UV light to induce a photochemical reaction that hardens a formulation. [626] UV curable products contain photoinitiators that, when exposed to UV energy, initiate a photochemical process that causes the polymers in the formulation to crosslink and harden. In UV curable compositions, there is usually no solvent to evaporate; instead, all of the liquid hardens through the crosslinking reaction. Very similar to thermal curing mechanisms for polymers described above, UV-activated photoinitiators can cause a polymeric binder resin to lock materials in place, increasing adhesion to the surface, and can supply connectivity throughout the formulation by crosslinking functional polymers.

UV curing is a rapid process that directs energy to a targeted location, and therefore uses less energy than thermal curing methods. [611] This allows for the use of more temperature sensitive substrates because the energy is directed at the formulation, not the entire system. Since UV curing is such a rapid process, it can be performed in-line and does not interrupt process flow or slow production. However, sometimes formulations cured with UV energy can suffer from inconsistent physical properties if they are improperly irradiated, and UV inks are much more sensitive to proper curing procedures compared to other curing methods. [627] The startup costs for a manufacturing plant intending to utilize UV curing mechanisms are higher because of the high cost of UV curing equipment compared to thermal ovens, for example. [628]

Because of its advantages and despite its disadvantages, UV curing is widely used throughout the flexible electronics industry. In fact, UV cured inks are one of the three broad categories of inks for printed electronics (the other two are aqueous and solvent-based). As mentioned in Section 3.3.2, UV inks can cure rapidly, making them advantageous for roll-to-roll environments. UV curing is used by a variety of industries besides the printed electronics industry, including automotive, telecommunications, and graphic arts. [626] Therefore, the list of companies that produce UV curing equipment is extensive, and most of the UV curing equipment that companies produce for other industries are suitable to cure the necessary components in a functional ink as well. However, there are some companies producing UV equipment that are specifically targeting printed electronics applications. These UV equipment companies and various information about them and the equipment they produce can be found in Table 19.

Table 19. Companies Offering Post-Treatment Equipment for Printed Electronics

Company	Headquarters	Post-Treatment Products
NovaCentrix	Texas	PulseForge photonic curing tools
Dresden Thin Film Technology	Germany (no U.S. location)	Ultra short time photonic annealing system using flash lamps
Xenon Corporation [365]	Massachusetts	RC-Series modular UV curing systems; Sinteron photonic sintering line; dual- stage pulsed light photonic curing system
Integrity [366]	New Hampshire	Official U.S. reseller of UK company Printed Electronics Ltd (PEL) UV LED curing system
Polymertronics [367]	United Kingdom (no U.S. location)	Jet ray and LED UV curing systems for R&D applications
Heraeus Noblelight Fusion UV [368]	Maryland	UV curing systems for electronics
Nordson [369]	Ohio	Industrial microwave-powered UV curing equipment
Heraeus Noblelight [370]	Germany (U.S. location in Georgia)	IR heating systems for printed electronics; UV curing systems for surfaces and printed inks
Nordson Asymtek [371]	California	Inline UV curing ovens for conformal coating; IR convection ovens for conformal coating
Adphos [372]	Germany (U.S. location in Wisconsin)	L-Series NIR drying/curing/sintering systems

Oftentimes, UV curing and EB curing are grouped together under the umbrella of radiation curing techniques (even though IR is also a form of radiation, it is not typically grouped with these two). [636] While UV curing uses photons as its energy particle and that energy activates a photoinitiator, EB curing uses electrons and the electrons themselves initiate crosslinking without the use of a photoinitiator. [637] EB curing has been briefly mentioned in literature as a method for curing printed electronics inks, but not much evidence has been found to demonstrate its success until recently. [638] In June 2014, Fraunhofer Institute released a poster describing the EB sintering of copper inks for printed electronics applications. [639] They describe using an Aerosol Jet printer to print copper ink onto polymeric substrates, which were then sintered using a focused EB. Their conclusions suggest that EB curing can be used for a variety of FHE technologies, but no other information can be readily found regarding the use of EB curing for printed electronics applications.

4.1.3.4 IR Curing

Similar to thermal curing, IR curing functions by removing and/or changing components in an ink composition. IR curing techniques use IR energy to induce molecular motion, which leads to heating of the molecules and overall formulation. [611] Then, similar to the mechanisms involved with thermal curing, the heat causes the liquid carrier to evaporate or activates a thermal initiator to crosslink polymeric components. [640]

IR curing offers benefits over UV curing because IR wavelengths can penetrate many different substrates, including ones that are visually opaque, while UV energy can only penetrate UV transparent substrates. [611] IR radiation allows heat to be delivered in exact amounts directly to a specific location, minimizing the concern for thermally sensitive substrates. However, since IR curing is a line-of-sight technology, it only delivers heat to a surface that it is directly facing.

[641] Therefore, products with curved surfaces become more difficult to cure, and if the printed ink is a thick film, only the top few layers will be subject to curing.

Similar to UV curing, IR heating is used by a variety of industries, including the everyday consumer. IR ovens are often sought out as an alternative to conventional thermal ovens used in industry because they lead to shorter cure times and require less floor space. [642] Therefore, just like with the UV technology, countless companies are invested in producing IR equipment, but only a couple directly target printed electronics applications. These few companies are described in Table 19.

One of these companies, Adphos, which is headquartered in Germany with a U.S. location in Wisconsin, appears to be the leader in IR curing technology for flexible electronics applications. Several examples of universities and companies that use their technology can be found throughout the literature. For example, in March 2012, a patent was granted to German company Osram Opto Semiconductors, for an encapsulation method for organic devices. [643] In their patent, they describe a process to fabricate an OLED which includes using a bonding material that is IR cured, and they identify Adphos as a manufacturer of the IR technology. Additionally, researchers from Swansea University in the United Kingdom published a paper in June 2014 detailing their ultrafast NIR curing method for PEDOT:PSS for flexible electronics applications. [644] They describe how the cure time of a PEDOT:PSS solution was able to decrease from 240 seconds to 2 seconds using IR curing methods, and the underlying polymeric substrates were left undamaged during the process. This research group took advantage of Adphos' technology in order to perform their work.

4.1.3.5 Chemical Methods

Chemicals and chemical reactions can be used to change, add, or remove components from a printed electronics ink formulation, leading to enhanced functionality.

As described above, heat, UV, and IR curing methods can induce chemicals, known as initiators, to begin crosslinking and hardening an ink formulation. However, an additional energy source in the form of heat, UV, and IR is not always necessary to cause crosslinking, and instead curing can be induced simply from the introduction of chemicals. For example, as mentioned in the description of conductive epoxies, in a two-part conductive epoxy system, a curing agent is added to a binder just before application to initiate the crosslinking reaction, without the need for an external energy source. The two components of the system are simply mixed together to cause the structure to change, ultimately leading to the designed functionality of the ink.

The full functionality of a formulation can be realized simply by adding materials to the composition during the post-treatment step. For example, chemicals can be added to improve the conductivity of compositions, which is referred to as doping. Carbon-based inks take advantage of this process by doping the carbon components, including CNTs and graphene, with various materials, as demonstrated by researchers from the Singapore Institute of Manufacturing Technology in 2013. [645] CNTs can be doped with electron acceptors like bromine or electron donors such as potassium in order to reach an acceptable level of conductivity. Graphene is a better conductor than CNTs by design, but it can still be doped with wet chemicals like nitric acid in nitromethane in order to be more useful in high performance applications.

Finally, materials can also be removed from a composition through a chemical process. In addition to being removed through heat treatment, ligands can be removed through a chemical mechanism, where the printed inks are exposed to a chemical reagent that would either remove the ligand or exchange it with shorter molecules that would less hinder functionality. [607] Removing a ligand through chemical reaction is applicable to any printed electronics ink that contains a ligand structure, including nanoparticle compositions and formulations using ligand-based additives.

4.1.3.6 Sintering

Similarly to how the various curing methods previously discussed cause polymeric materials in a formulation to physically and chemically combine to produce continuous connectivity, sintering provides a way to connect particulate components, specifically metal particles, in a functional formulation. Sintering is a type of curing that involves heating particles to near but still below their melting point so that the molecules can diffuse across particle boundaries to become one solid mass. [646] This process is important in order to ensure continuous connectivity is established through the particles within the formulation, which allows the formulation to function as designed. For example, continuous connectivity can lead to increased electrical conductivity as it gives a connected path for the electronics to travel. Various sintering methods exist, including thermal, photonic, microwave, plasma, electrical, chemical, and laser. While liquids or other components may be evaporated or removed due to the energy applied to cause sintering, this is simply a byproduct of the mechanism, and sintering strictly refers to the diffusion of molecules across particle boundaries to become one continuous material. In fact, this byproduct of removing other components is beneficial because the other components may need to be removed before the ink can be efficiently sintered.

4.1.3.6.1 Thermal

Thermal sintering is the conventional method used for sintering materials, and it involves heating the ink to drive off unwanted liquids/components and force the particles to become closer to each other. [428] Through sintering, thermal energy allows the particles to diffuse together to form a continuous functional path at temperatures below the particles' melting points. Nano sized particles tend to have reduced melting points because of their large surface-to-volume ratio (the melting point of bulk gold, 1063 °C, decreases to 380 °C for 1.5 nm particles). [428] Despite this extreme reduction, not much evidence exists for a conductive pattern (with acceptable conductivity levels) that resulted from sintering at temperatures below 150 °C, and usually heating to a high temperature (300 °C and above) is required to eliminate all the undesired organic components that get in the way of the sintering mechanisms. High temperatures can cause problems for temperature sensitive substrates, which are becoming more popular for printed and flexible electronics. Therefore, significant emphasis is being placed on alternative sintering methods in academia and industry that do not require the system to be exposed to such high temperatures.

4.1.3.6.2 Photonic/Laser

Photonic sintering operates under the same mechanisms as photonic curing described above, but is specifically designed to cause metal particles to diffuse together into a solid network, as opposed to causing polymers to crosslink. Photonic sintering is similar to thermal sintering in that it eventually results in heating of the printed metallic layer and evaporation of the undesired

liquids. [428] However, instead of the source of energy being thermal, the printed conductive layer absorbs light from a flashlamp, which leads to heating as the molecules start moving more rapidly. The volatile liquid carrier in the ink evaporates, and the particles are melted and sintered together forming a continuous line. [647] This method is desirable because the energy transfer is more selective, resulting in a smaller heating zone and making this approach applicable to systems with plastic substrates.

Low-temperature laser sintering can be used to induce continuous functionality in formulations, and it functions almost identically to photonic sintering, with the only difference being the use of a laser instead of a flashlamp. [647] The particles in the ink are heated as they absorb incoming laser radiation. The liquid carrier heats up and evaporates, and the functional particles are melted and sintered together. The intensity of the laser affects the final properties of the ink, and the curing process is driven primarily by the heat diffusion initialized by the laser. This method is desirable because it primarily heats the particles, and therefore temperature-sensitive substrates can be used. However, the smaller heating zone could make it more difficult to apply this method to large areas, such as PVs. [648]

Photonic and laser sintering seem to be the most commonly researched alternative sintering methods. UCLA, University of California at Berkeley, and North Dakota State University are heavily invested into these research areas. Outside of the United States, Hanyang University (Korea), Korea Institute of Science & Technology, Swiss Federal Institute of Technology (Switzerland), The Hebrew University of Jerusalem (Israel), Osaka University (Japan), Wroclaw University of Technology (Poland), Tampere University of Technology (Finland), Friedrich-Schiller-University Jena (Germany), and the Dutch Polymer Institute (Netherlands) are all researching photonic and/or laser sintering methods for FHE applications.

In addition to universities, several companies are developing or already offering alternative sintering equipment for printed electronics applications. Smit Ovens, located in the Netherlands, has developed selective photonic sintering technology that uses wavelengths that are absorbed by the ink but are transparent to the substrate. [649] This pulsed light technology is also much faster than thermal oven sintering, which allows for decreased processing time. They are currently focusing on sintering silver nanoparticle inks, and they with their technology can achieve 12 percent of the bulk conductivity of silver.

Smit Ovens is also performing experiments to understand substrate deformation and ink adhesion and how these variables are affected by their photonic sintering technology. [649] As part of their experimentation, they defined a quantifiable variable called substrate deformation angle, which is the angle the substrate makes with a horizontal surface when it curls up due to deformation. They also measured expansion and shrinkage of the substrate. As a result of their studies, Smit Ovens found that the deformation angle is strongly dependent on the ink formulation, substrate composition, and photonic flashing conditions. They have also discovered that there is not a significant difference between thermally and photonically sintered inks with regards to adhesion, and that both methods lead to acceptable levels of adhesion. However, they did determine that if the structure encounters bending or flexing, the thermally sintered samples degrade faster than the photonically sintered samples.

In Table 20 is a list of companies offering sintering equipment based on alternative sintering methods. As can be seen, all except one company on the list offers products that function through photonic mechanisms. At this time, it appears that microwave, plasma, and electrical sintering methods are still being researched strictly in universities, and have yet to reach the commercial market. A brief description of these new methods is in the subsequent paragraphs, but significant detailed information could not be found regarding these techniques.

Table 20. Companies Offering Alternative Sintering Products

Company	Headquarters	Type of Sintering	Product Name/Description
Neotech AMT [650]	Germany (no U.S. location)	Photonic	LBS 45XE – light beam photonic sintering system
Xenon Corporation [616]	Massachusetts	Photonic	Sinteron Series – pulsed light sintering systems ranging from benchtop to roll-to- roll production sized models
NovaCentrix [615]	Texas	Photonic	PulseForge Series – photonic curing/sintering systems ranging from R&D to production sized models
Smit Ovens	Netherlands (no U.S. location)	Photonic	Selective photonic sintering technology and large area drying for sheet-to-sheet and roll- to-roll formats
Coatema [651]	Germany (service location in U.S.)	IR	Several sintering systems which use IR sintering methods
Adphos [635]	Germany (U.S. location in Wisconsin)	IR	L-Series – family of drying/curing/sintering systems that uses NIR technology
Intrinsiq Materials [652]	New York	Laser	LAPS-60 – IR laser sintering system, plus additional laser sintering systems for lab scale and developmental efforts
Heraeus Noblelight [633, 653]	Germany (U.S. locations in Georgia)	IR	Tailored IR tool for drying and sintering processes in printed electronics
Mitsubishi Imaging (MPM), Inc. [654, 655]	New York	Chemical	Mitsubishi NanoBenefit 3G Series – silver nano ink and silver nano inkjet media that possess proprietary chemical sintering agents

4.1.3.6.3 Microwave

Microwave sintering is relatively new to printed electronics. Microwave radiation has recently been proven to sinter metals, but the radiation has a very small penetration depth. [428] Therefore, the printed layer needs to be very small in dimension. Because most inkjet printed tracks satisfy this requirement, it is expected that this sintering method will become more popular for industrial manufacturing. Friedrich-Schiller-University Jena (Germany), Eindhoven University of Technology (Netherlands), and the Dutch Polymer Institute (Netherlands) are all researching microwave sintering methods.

4.1.3.6.4 Plasma

While not much information is available on plasma sintering, it has proven to be applicable to conductive inks containing both metal nanoparticles and metal complexes. [428] The metals in

the printed patterns meld together through exposure to low pressure argon plasma and electron-cyclotron resonance (ECR) plasma. This method can be carried out on temperature sensitive substrates, but sometimes has a negative effect when organic materials are involved. [656] Eindhoven University of Technology (Netherlands), Dutch Polymer Institute (Netherlands) Chemnitz University of Technology (Germany), Fraunhofer Institute for Electronic Nanosystems (ENAS) (Germany), and Friedrich-Schiller-University Jena (Germany) are all invested in researching plasma sintering methods for printed electronics applications.

In 2006, Optomec filed a patent application entitled "Method and Apparatus for Low-Temperature Plasma Sintering" which described a method of removing organic material from a metallic nanoparticle conductive ink and sintering the metallic particles, using plasma instead of high temperatures. [657] However, it does not appear that Optomec offers any products to date that harness this sintering technology that was granted a patent in 2007.

4.1.3.6.5 Electrical

Similar to the thermal and photonic approaches where the main mechanisms for sintering involve heating of the metal layer, electrical sintering involves heating by applying a voltage that induces current flow through the structure. [428] The heating then causes the metal particles to diffuse together and become one solid mass. This method is desirable because it happens quickly and does not allow for overheating of the substrate. The research for this sintering method is being led by VTT Technical Research Centre of Finland.

4.1.3.6.6 Chemical

A new approach to sintering is through chemical agents used at room temperature. [428] When an oppositely charged polyelectrolyte comes in contact with a metal nanoparticle, it was discovered that these particles undergo a spontaneous coalescence process that makes achieving high conductivities possible at room temperature. This discovery is being researched at the Hebrew University of Jerusalem.

4.1.3.6.7 Advantages/Disadvantages of Sintering Methods

The main disadvantage of traditional thermal sintering methods is the high temperature necessary to achieve acceptable electrical conductivity. [428] On conventional electrical substrates like glass, ceramics, and silicon wafers, the high temperatures necessary (sometimes 300 °C or higher) are not an issue. [658] However, the new substrates that are being used in flexible electronics, often polymeric like PET and polycarbonate (PC), cannot withstand these high temperatures. Some of these materials can only be heated to around 150 °C, which is not even high enough for some of the unwanted liquids in the ink to evaporate. Therefore the majority of these other methods present ways to produce adequate conductivity without having to reach high temperatures, which is their main advantage compared to thermal sintering. Table 21 gives more detailed information about the advantages and disadvantages of the various sintering methods. Additionally, as shown above, the majority of the research being performed on alternative sintering methods is taking place outside of the United States, and mainly in Germany and the Netherlands.

Table 21. Advantages and Disadvantages of Various Sintering Methods

Method	Advantages	Disadvantages
Thermal	Traditional method used, so there is significant research behind the already established processes [428]	High temperatures necessary to fully sinter can damage temperature sensitive substrates [428]
Photonic/Laser	Smaller and directed heating zone allows for a wider range of substrates to be used [647]	Costly and complex process, as it requires sophisticated systems; very direct heating results in difficulty to cover large areas [648]
Microwave	Fast sintering times, simple, cost effective [659]	Radiation has a small penetration depth, which could lead to non- uniform sintering [659]
Plasma	Can be carried out on thermally sensitive substrates [428]	Application of plasma at low pressure can have negative effects on organic materials [656]
Electrical	Extremely quick method which does not allow for overheating of the substrates [428]	Cannot reach as high of conductivities as traditional thermal sintering methods [660]
Chemical	Sintering possible at room temperature [428]	Messier and potentially more hazardous process since it involves the use of chemicals [428]

4.1.4. Metrology, Process Control, and Quality Control

Process control, metrology and quality control are all standalone critical parts of the manufacturing of printed flexible electronics. Process control deals with the hardware and software needed to regulate and control manufacturing processes. Examples of these controlled manufacturing variables include machine speed, web tension, web alignment, nozzle pressure, vibration, and so on. Metrology deals with the optical inspection of the manufacturing process to control and minimize defects in products. And quality control involves testing of a work in process or completed product, which is usually compared to a standard. All three of these components of the manufacturing process are intimately linked, and the outcome of any one of them will affect the others.

Metrology for FHE is a very broad subject that deals with every step in the manufacturing process, and in some respects it can encompass parts of process and quality control as well. It ranges from substrate quality and defects to end of the line continuity testing of finished electronic components. Metrology in printed electronics is very critical due to cost of the raw materials being used to make the products, such as substrates and inks, and the scale of the devices being in the nano and micro meter range. Improving upon current metrology technologies is approach to metrology for roll-to-roll processes. As devices get smaller and smaller, current metrology technology might not be applicable, and the ability to test these nano-scale devices end to end will be a challenge that will need to be met. Controlling the manufacturing process will be completely dependent on data and feedback received from metrology systems and quality control testing. Precise and reliable metrology will be the key to a well-functioning FHE manufacturing line.

Although systems currently exist that measure and correct roll-to-roll manufacturing systems, the nano-scale nature of printed electronics forces the need for new hardware and software requirements to detect and control the various defects that can occur. Almost every area within

the FHE manufacturing process can lead to defects. Printing defects can lead to open or short circuits. Substrates can also have defects from the manufacturing process, or there can be particles on the surface of the substrate, which can cause printing errors. The electronics manufacturing process itself can also cause defects. Being able to control and account for these defects is extremely important in the manufacturing of printed electronics.

Printing defects are caused by missing or disconnected patterns, which, as mentioned previously, can unfortunately cause open or short circuits. The defects can be caused by missing or clogged nozzles, deviating nozzles, a variety of mechanical machine issues, such as web wander and vibration, and particle contamination on the application roller or stamp. Web wander is the movement of the web in a sideways motion perpendicular to the machine direction, which can cause some areas on the substrate to receive more ink and other areas to have no ink at all, as depicted in Figure 30. [661, 662] Although all of these root causes are very different in nature, they all cause printing defects that could lead to loss of product.

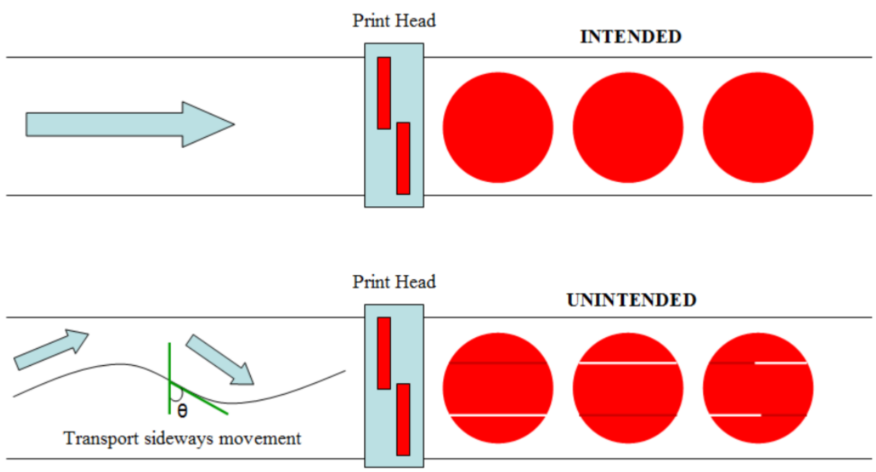


Figure 30. Demonstration of Effects of Web Wander [661]

Registration control is a big challenge facing the printed electronics industry. Registration refers to recognizing where ink needs to be laid in order to create a viable product. It is crucial to have precise registration as the substrate moves from one print station to the next, regardless of how the ink is deposited. Due to the nano/micro-scale manufacturing of printed electronics, current tools are inadequate for the tight registration requirements. Accuracy of the ink placement is impacted by several factors, including drop velocity. If two droplets are fired from the print head at the same velocity, they will land at the same place on the substrate. However, if the velocity of the droplets differs ever so slightly and the web is moving at a high rate of speed, the droplets will be displaced on the substrate, therefore affecting registration. Other factors that affect registration accuracy include web transport stability and misalignments. New hardware and software tools need to be developed for in-line systems to detect these types of manufacturing defects and provide for automatic correction.

Researchers at the University of Texas at Austin, University of Michigan, and Omega Optics, Inc have developed a metrology tool specifically for FHE. Their technology visually observes an alignment mark on the substrate at high web speeds and provides error in position information. An alignment mark, such as a cross, is printed along with each functional ink layer. High speed

cameras observe the specific alignment marks that are printed along with the electronic circuits. The image alignment marks are compared to a set of standard patterns preloaded into the computer software, and the misalignment coordinates in terms of x, y, and rotation are calculated and displayed. Figure 31 denotes typical lateral, longitudinal and angular offsets that can be observed. This information is fed back to the controller and printer in order to correct for the deviation in-line, and allow automatic inline registration. The power of the camera and software threshold is dependent on how precise the registration needs to be.

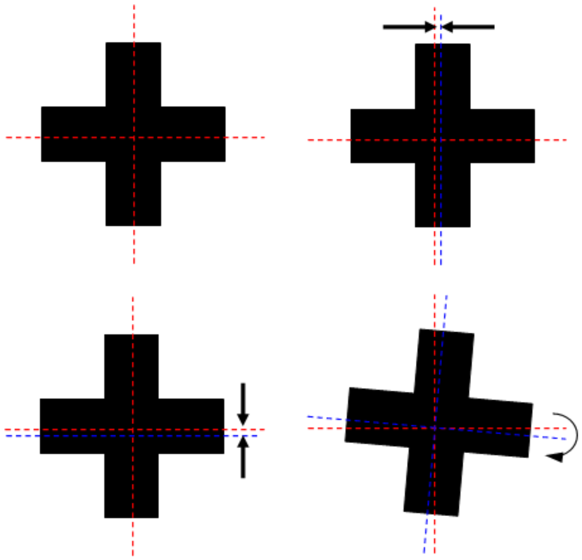


Figure 31. Examples of Alignment Marks from New FHE Metrology Tool [661]

Although substrates are described in Section 3.4, it is important to discuss substrate quality with respect to metrology. The particular substrate selected can have a direct impact on type of defects that are observed. There are several characteristics of substrates that affect quality, including surface roughness, surface energy, chemical and moisture resistance, high temperature behavior, and transparency. Surface roughness is perhaps the most critical substrate parameter regarding metrology for the printing process because it will affect how the ink is accepted by the substrate. Proper choice of substrate is highly dependent on the ultimate application and printing process.

Outside of printing and substrate defects, static is an inherent problem in manufacturing of any rolled substrate material. Static can also be picked up from simple handling of the substrate. If static exists on a substrate at the time of production, it can pull particles and contaminants from the manufacturing environment onto the substrate. Static can also have an effect on material deposition accuracy, as charged ink can be pushed or pulled to an undesired location on the substrate due to static. [663] Static is a universal problem in printing and roll-to-roll production, and therefore some solutions already exist. Particles that were attracted to the substrate due to static can be removed in a pretreatment process called web cleaning (see Section 4.1.1.3). Static can also be controlled by increasing humidity. Unfortunately, static is cumulative in nature. It starts at a relatively low voltage at the beginning of the process, but builds as the substrate travels over each subsequent roll. If the charge builds up enough, such as to 10,000V or more, it can damage the surface of the substrate as it discharges. The printing community has long dealt with

static problems, and simple technologies and equipment exist to account for static charge. Simco-Ion Industrial Static Control in Hatfield, PA, is one such company and has various products that control static in industrial environments, including static neutralizing systems and static charging systems. [664]

With the revolution of roll-to-roll printing of electronics, there exists a need to enhance current metrology methods or develop new, sound metrology methods. Surface defects can be costly in printed electronics with the cost of raw materials alone. Surface roughness can have an effect on the longevity of components deposited on to a flexible substrate. Misalignment of a substrate as it travels through a printing station can also have a large economic impact. Metrology methods need to be fast, as a roll-to-roll system is constantly moving at relatively high speed. Other necessary qualities in a roll-to-roll metrology system include: in-line compatibility, simplicity, lightweight, non-contact, and non-destructive. [665] Inspection and quality control are of great importance in roll-to-roll manufacturing. To have a successful outcome, issues such as defect detection, surface roughness, layer quality, electrical properties, registration control, repair / correction, product testing, and flex testing need to be monitored, controlled, and tested. [665]

One type of metrology is ellipsometry, which measures a change in polarization as light reflects or transmits from a material structure. The polarization change is represented as an amplitude ratio and phase difference. The measured response depends on optical properties and thickness of individual materials. Thus, ellipsometry is primarily used to determine film thickness and optical constants. It is also applied to characterize composition, crystallinity, roughness, doping concentration, and other material properties associated with a change in optical response. [666]

Ellipsometry has numerous advantages compared to standard reflection intensity measurements, such as the capability to measure up to 16 parameters at each wavelength, being less affected by intensity instabilities of the light source or atmospheric absorption, and not needing a reference measurement. [667]

There are several companies and universities that are working with ellipsometry, and among the leaders in the U.S. is J.A. Woollam Company in Lincoln, NE, which is a product of research conducted by Dr. John A. Woollam at the University of Nebraska. The company has a large offering of metrology devices that utilize ellipsometry techniques, and is currently working on an inline system for roll-to-roll applications. Other companies providing ellipsometry metrology solutions include Gaertner Scientific Group, in Skokie, IL, and Angstrom Advanced Inc. in Braintree, MA.

Dark Field Technologies in Orange, CT, has developed a metrology technique called Solid State Laser Reflection (SSLR). This technology addresses problems typically associated with FHE manufacturing, such as visual inspections being difficult due to high line speeds and the requirement to visually observe 10-100µm defects. Other problems include correlating defects to a root cause, especially if a substrate has multiple coatings. The biggest issue to substrate and coating metrology is the reflection challenge, which is where small changes in reflection angles caused by bounce/flutter or deviations from flatness defeat conventional inspection systems. [668] Conventional inspection methods are typically not reliable because they require continual adjustment to misalignment, may require shrouding, and are expensive and difficult to maintain.

Dark Field Technologies' SSLR system addresses all of these inspection issues for coated films and glass. The SSLR system is a self-aligning system that compensates for the vibration produced by manufacturing machines. Other benefits include ease of installation, ease of access to the line, and maintenance and tuning being performed on an annual basis. SSLR metrology technology provides an advantage because light interacts with the defect twice. Therefore, the SSLR systems have successfully detected repeat coating defects on reflective film, bumps or topographic defects, scratches, and coating pin holes. This technology has been developed for use in both in-line on a roll-to-roll machine and in a benchtop laboratory setting.

Another pioneer company in the field of roll-to-roll metrology is 4D Technology Corporation, based in Tucson, Arizona. [669] They manufacture optical metrology systems, and their newest offering, FlexCam module, has recently been introduced to the market. FlexCam is a compact, high resolution 3D metrology system for flexible electronics. While only the top surface of the material is measured by this technology, it can be placed in-line on a roll-to-roll process and can provide sub-nanometer vertical resolution and micro-meter lateral resolution to detect surface roughness and quantify defect measurements for substrates, barrier films, or multicoated substrates. Problems such as runout (web speed increasing when nearing the end of a roll), web flutter, vibration, and others do not affect the accuracy of the measurements with this system.

With the FlexCam system, defects are identified and quantified, and their position within the roll is documented. [669] Multiple defect statistics are calculated and operators can select pass/fail criteria based on area, volume, depth, and slope of the defect that might affect long term performance. Root cause of a defect can be determined by comparing extrinsic and intrinsic defects. The FlexCam can provide continuous inspection for web speeds up to one meter/minute (which is compatible with the speeds at which FHE are manufactured), and multiple units can be lined up across the web to sample the desired area. All data processing is on-board and thus has real time feedback.

These are just three examples of companies using different metrology technologies to address roll-to-roll defect detection. The specific technology that is used in any given scenario will depend on the particular materials, manufacturing process, and FHE product being produced for the desired application.

Closely related to metrology and process control, quality control is used to ensure a certain level of quality in a product [670], and for printed electronics, this mean testing of electronic devices at every level and stage of production. For example, substrates need a certain surface roughness, and inks need to have certain viscosities under specific operating conditions. Finished products such as transistors will need to switch at desired speeds. All of these measurements will be obtained by quality control testing. Preliminary quality testing can help identify the best materials to make any given electrical component, based on operating environment and end use. Quality control techniques can also help identify why devices fail. Overall, quality control is a required link in the manufacturing chain to ensure reliable FHE products.

Because FHE encompasses countless different technologies, the types of quality control testing that will be performed for FHE are very broad. Therefore, it is helpful to study examples of groups that employed various quality control methods for FHE in order to get a glimpse into the

different technologies that are used. One such example comes from researchers working at the National Institute of Standards and Technology (NIST), the University of Maryland, and Sandia National Laboratories. They, for the first time, successfully imaged the inner workings of experimental solid-state flexible batteries as they charged and discharged, while making detailed measurements of their electrochemical health. [671] Their imaging technique can be used with any solid state battery. It combines a number of different tools including photoelectron spectroscopy, scanning electron microscopy (SEM), and Auger electron spectroscopy (AES) under high vacuum. The setup enabled the team to precisely control the lithium reaction rate, the battery state-of-charge and state-of-discharge, record the electrochemical potential, and correlate these parameters with specific changes in the electrode's structure and chemical composition.

Photoelectron spectroscopy utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface of a sample. [672] High resolution photoelectron studies can now be accomplished with synchrotron radiation sources. These studies are enabled by radiation spanning a much wider and more complete energy range (5 – 5000+ eV). However, there are limited numbers of these high resolution sources, and due to the expense and complexity of testing, only a small amount of high resolution photoelectron spectroscopy is being completed.

A scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. [673] The signals that derive from electron-sample interactions reveal information about the sample, including external morphology, chemical composition, crystalline structure, and materials orientation.

AES is a common analytical technique, specifically in the study of surfaces. [674] Underlying the spectroscopic technique is the Auger effect, which is a phenomenon where energetic electrons are emitted from an excited atom after a series of internal relaxation events. AES has become a practical and straightforward characterization technique for probing chemical and compositional surface environments and has found applications in metallurgy, gas-phase chemistry, and throughout the microelectronics industry.

All three techniques, photoelectron spectroscopy, SEM, and AES, can be used for quality control purposes for FHE, outside of flexible solid-state batteries.

Along with research institutions, companies are also involved in researching quality control methods for FHE. Hysitron, a privately held company in Minneapolis, Minnesota, is the world leader in mechanical test equipment for nano- to microscale mechanical and electrical testing. [675] Since 1992, they have created systems that measure mechanical and electrical properties of metals, polymers, ceramics, and composite materials on both bulk materials and coatings, primarily for the aerospace, electronics, and semiconductor industries. They both sell equipment to customers and also have a laboratory where they can run tests on material samples for customers.

Overall, Hysitron's equipment allows users to understand how the mechanical properties of a material change as the material becomes thinner. At the heart of Hysitron equipment is their patented three-plate transducer and probe that can perform nanoindentation, scratch, and wear

testing to determine material characteristics at the nano level, such as hardness, creep, modulus, and adhesion. Hysitron's equipment can measure mechanical properties in both static and dynamic modes, and has a temperature range of approximately -17 – 800 °C. In addition to its measurement capabilities, Hysitron's equipment can be used as an imaging tool for surfaces. This capability allows them to create maps of a surface that can also display property data, such as modulus. A slight tweak to the three-plate transducer allows the equipment to measure electrical properties alongside mechanical properties. Because of this feature, electrical and mechanical data curves or maps can be gathered simultaneously.

One new feature that Hysitron is launching is a special interface that would allow their instruments to be compatible with Raman spectroscopy equipment. Hysitron is not selling Raman instruments, but instead have developed a fiber optics cable to connect their thermomechanical test equipment to a Raman spectrometer. This would allow a sample within the Hysitron equipment to be subjected to Raman spectroscopy as well, which would provide a chemical footprint of the material in addition to mechanical and electrical data.

Microelectronics packaging is one of the main areas where Hysitron's equipment is used. As microelectronics become smaller and denser, the thermomechanical and electrical characteristics of the materials that are used to create and package electronics become more important. These electronics systems contain various materials, including plastic, metal, ceramic, glass, and composite, all of which have different coefficients of thermal expansion. Therefore, the thermomechanical responses of these systems need to be extensively studied and tested in order to ensure that material stresses do not cause an overall system failure. Hysitron is hoping that its equipment can help to ascertain whether forces subjected to electronics systems during manufacturing and packaging are significant enough to ultimately affect performance. Understanding the electrical and thermomechanical forces involved with the packaging of electronics is necessary for both the conventional and flexible electronics industries.

Additionally, in flexible electronics, it is increasingly important to understand the properties of films that are being used as substrates and other materials that are being used for FHE that have not previously been used in conventional electronics manufacturing and packaging. Since Hysitron's systems are not compatible with roll-to-roll manufacturing, and they currently do not have the capabilities to monitor products in real time on a production line. Instead, their equipment will be used mainly in a product development and/or quality control environment for the flexible electronics industry. Overall, Hysitron is involved in a niche market and therefore does not have a significant amount of competition. However, what makes them different from other companies involved in thermomechanical test equipment is their ability to go down to the nano-scale, while most other companies are strictly focused at the micro-scale. This capability gives them an advantage in the electronics world, specifically regarding FHE.

Regarding metrology, process control, and quality control, the greatest hurdle to overcome for roll-to-roll printing of electronics is the ability to perform inline metrology on a nanoscale. Although some methods currently exist, the quality of metrology needed for inline scanning of a moving production line has not yet been achieved. Various companies and universities mentioned above are working toward this goal. Once reliable inline metrology systems are developed, inline process control technologies will follow. In a broad sense, the challenges to

overcome for manufacturing of FHE include moving production lines, nanoscale metrology of moving lines, and real-time feedback and correction. Along with these manufacturing goals, standards need to be established.

As described, metrology, process control, and quality control are extremely important considerations for manufacturing FHE. They allow for the manufacturer to control and minimize the amount of defects that find their way into the final electronics product, therefore increasing the performance and quality. Several companies, including the ones mentioned throughout this section, are already involved in these technologies specifically for FHE applications, and as more research is performed and FHE becomes more mainstream, it is probable that more companies with specialized process control, metrology, and quality control tools for FHE will emerge.

4.2 Manufacturing FHE with Conventional Electronics Manufacturing Methods

Conventional electronics manufacturing methods, which use silicon substrates and intensive lithographic processes to create high quality electronics, are a proven technology, and the infrastructure to create electronics through these methods already exists. Therefore, completely abandoning these conventional methods of producing electronics would not be feasible. However, the industry also recognizes the need for miniaturization and flexible electronics technologies in order to be competitive. Flexible electronics are desirable for multifunctional aircraft structures (i.e. conformal loadbearing antennas structures, fly-by-feel control, structural health monitor, etc.), and the previous sections have demonstrated that one way this can be achieved is through printing organic electronic inks onto flexible substrates. The problem with organic flexible electronics devices, however, is that they are much slower than their silicon counterparts. As mentioned, they are also sensitive to higher temperatures, and high-quality films are more difficult to achieve.

As an alternative to the methods of printing electronics described previously, many companies and universities are researching different ways to adapt conventional manufacturing methods to produce cost effective, high-performance, inorganic flexible electronics. A few of these innovative manufacturing techniques are discussed in the following paragraphs.

Today's silicon wafer ICs are considered bulky and are still quite stiff at 100 – 300 micrometers thick. [676] Thinner wafers, between 50-100 micrometers thickness, are so brittle they can fracture under their own weight. However, once the thickness transitions to below 50 micrometers, silicon becomes more stable and flexible. Below a thickness of 10 micrometers, silicon becomes optically transparent. These ultrathin (note: "ultrathin" is a widely used term in literature, but a standard thickness to define "ultrathin" has yet to be established), under 50 micrometer, electronics are suitable for thin film applications; they can be bent and twisted, and rolled up, and yet they remain strong with the desired characteristics that silicon provides.

Creating these ultrathin silicon chips is challenging. In conventional electronics manufacturing where chips are produced on top of a wafer roughly 750 microns in thickness, the actual functional electronic devices in an IC only occupy the top 5-10 µm of the silicon wafer. [676] Logically, the relatively thick portion of wafer material (the base layer) under the top functional electronics layer would need to be removed to create the ultrathin electronics. The base layer could be reduced using standard techniques of grinding, where the underside of the silicon

device is slowly ground down and removed until the desired thickness is met. However, this is a highly subtractive technique which wastes up to 99% of the silicon. The grinding techniques can also produce crystalline defects and cracks on the edges of the devices, leading to device failures. When it is desired for the electronics to be thinner than 50µm, this reduction grinding technique becomes cost prohibitive. Therefore, there is a need within the electronics industry to develop new manufacturing methods for creating ultrathin conventional silicon electronics. The driving factors for these new methods are cost effectiveness and the need for additive processes.

New silicon exfoliation techniques convert rigid silicon electronic devices into flexible ones that could be worn or rolled up. [677, 678] This new process involves electronic devices first being created on rigid silicon wafers using traditional methods, and then being exfoliated from the rigid wafer to form flexible silicon electronic devices. This process is extremely different from the fabrication of flexible electronics by depositing organic semiconductors on plastic film substrates, and it results in higher performing devices. A few research groups have begun to utilize these new techniques.

At King Abdullah University of Science and Technology, Muhammad M. Hussain and fellow researchers [677] have developed a cost effective, novel process that utilizes the most common form of silicon used by the electronic industry - monocrystalline silicon wafer. This process was later implemented with polycrystalline and amorphous silicon. Figure 32 demonstrates the fabrication process of flexible silicon electronics from rigid wafers, which increases yield and reduces cost. After the silicon wafer is prepared, the devices are created using standard lithographic methods. A thin silicon dioxide film is then deposited over the entire wafer to protect the fabricated device during subsequent processing. Photolithography and reactive ion etching is used to create 5 µm pores that bore through the oxide film, approximately 20 µm into the silicon. The entire wafer is then exposed to xenon difluoride gas which passes through the pores and etches away an entire layer of the silicon just micrometers below the wafer's surface. This etching then allows for an ultrathin layer of silicon, which is carrying the device, to be released from the silicon wafer. The remaining wafer can then be prepared for reuse and returned to the beginning of the process.

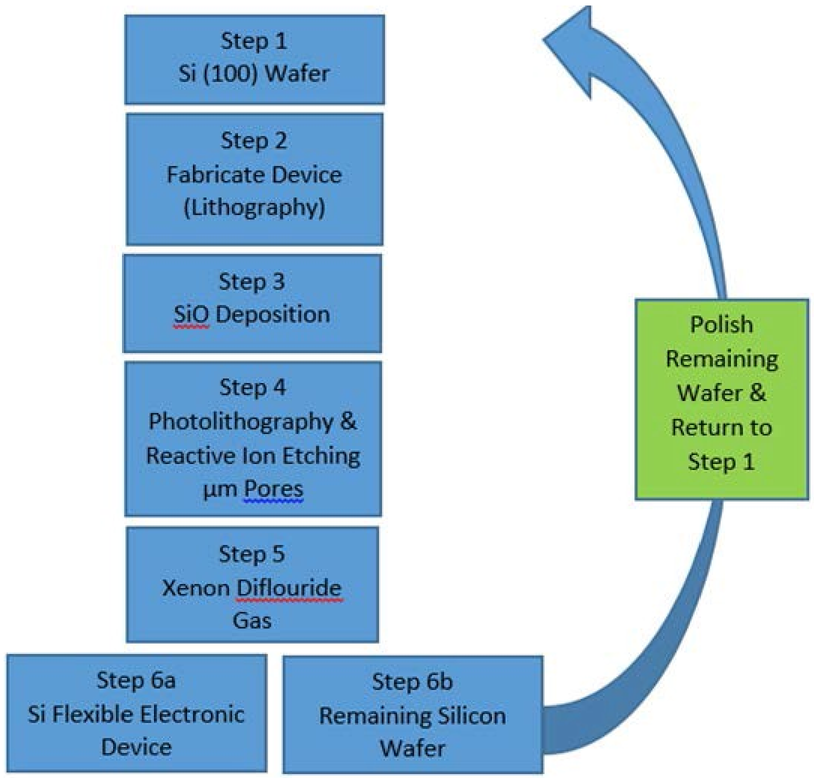


Figure 32. Flexible Si Electronics Device Fabrication Process [677]

This processing technique enables the creation of more flexible devices from the same wafer. This characteristic makes it an attractive cost effective process for the industry, which was the research team's main motivation, in addition to advancing the field of FHE. [679] This team has used their process to make bendable capacitors, transistors, lithium-ion batteries, and devices that convert heat into electricity.

The technology previously discussed involves flexible silicon electronic devices that are fabricated on top of a silicon wafer and then separated from the bulk silicon wafer in some fashion. These technologies are stable, and do not require the use of an additional support substrate, such as a polymer film, after being separated from the bulk silicon wafer. However, these processing methods are not yet well established in the industry. Today, a majority of flexible silicon electronic devices are manufactured by creating the device on top of a substrate other than a silicon wafer, such as a polymer film. The state of this industry is well established and capable of producing flexible silicon devices below 10 µm.

The recent developments by Hussain and his team of researchers described above could possibly replace current state-of-the-art production of flexible silicon devices on support substrates in the future. [677] However, Hussain would have to address the thickness of his technology, as it is approximately 125 times thicker than FleX™ Silicon-on-Polymer™, a proprietary manufacturing process (described below) developed by American Semiconductor. [680] It is expected that the development of pure silicon flexible devices from low cost bulk silicon substrates will be well established by 2021, possibly replacing current methods of adding a plastic or mechanical substrate.

American Semiconductor Inc. develops flexible ICs and flexible hybrid systems. As mentioned, they have developed the FleX Silicon-on-Polymer process, which creates high performance, single crystalline CMOS on a flexible substrate. This technology allows for a final silicon device thickness of less than 2000 angstroms, located on top of a polymer substrate. [680] The FleX process, depicted in Figure 33, is a post-fabrication method that can be applied to any silicon-on-insulator (SOI) wafer.

To begin this process, conventional electronics manufacturing methods are used to create the circuitry on an SOI wafer. A polymer is then applied on top of the circuit, and a carrier substrate is laid on top of the polymer layer. Through proprietary methods, the original SOI substrate, followed by the carrier substrate, is then removed to leave the thin silicon circuitry layer attached to a polymer layer.

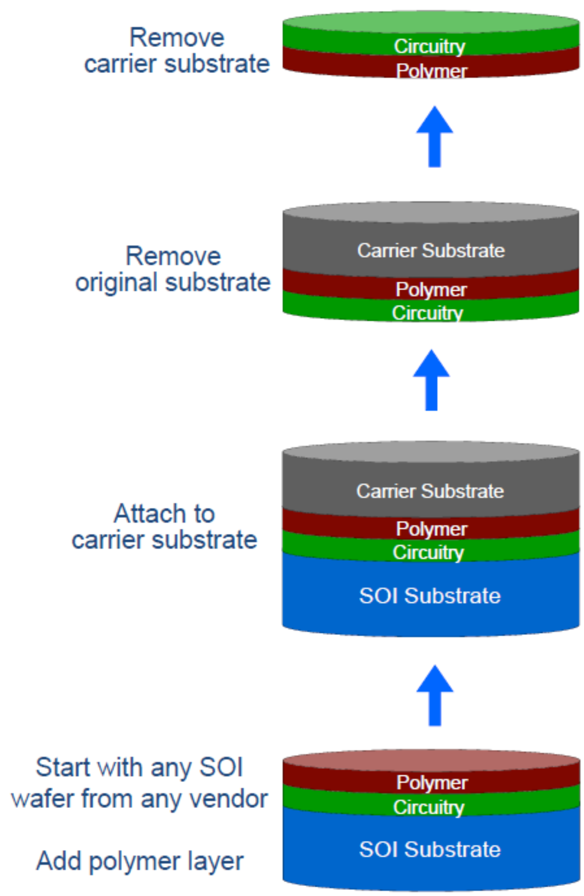


Figure 33. FleX™ Process Flow [681])

At the Institute for Microelectronics in Stuttgart, Germany, researchers have developed an ultrathin silicon chip process called ChipFilm™. [7] This process, depicted in Figure 34, involves growing a layer of crystalline silicon on top of silicon anchors, which ensure the foundation is strong enough for the fabrication but weak enough to allow removal of the finished chip. [676] To begin the process, the anchors are fabricated on a base/carrier silicon wafer by etching a 1µm thick layer of porous silicon. Underneath this layer, a 200 nanometer layer of coarser, porous silicon is also etched. The two porous layers are then sintered together at high

temperature to result in a continuous cavity containing vertical pillars. The pillar surfaces serve as seeds from which the ultrathin crystalline silicon is grown to the desired thickness over the entire wafer surface. With this process, silicon thicknesses of 10µm have been achieved. After the ultrathin silicon layer is grown, the chip goes through the traditional processing methods to create the desired electronics component. After the electronics are fabricated, deep trenches, which reach down into the cavity layer, are etched at the edges of each chip. At this point, the chip is only attached to the base silicon wafer by the vertical pillars. A pick and place tool is then used to grab the chip, using mechanical force to sever the chip from the anchors. The chips can then either be stacked or placed on to a flexible substrate to create a FHE device.

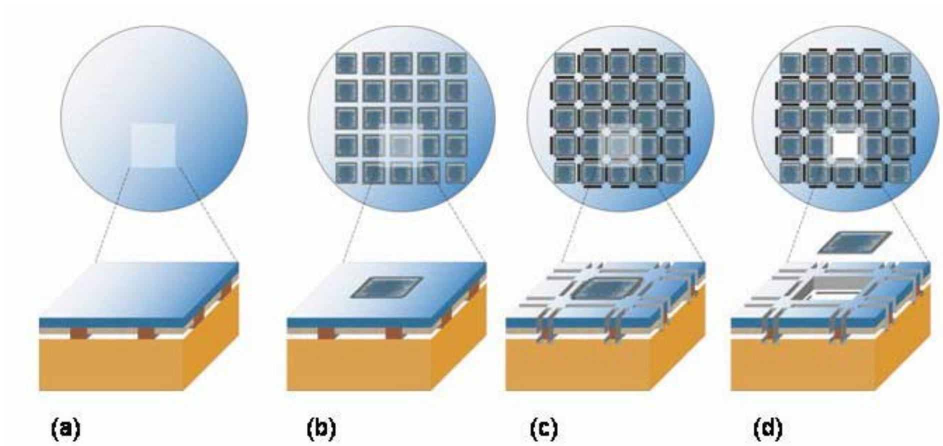


Figure 34. ChipFilm™ Process Flow [682]

The advantage to this manufacturing technique is that it is additive, and since the base wafer is only used as a carrier, after the process the remaining base silicon wafer can be ground down, polished, and recycled for future use. Unfortunately, there are also some challenges to be overcome with this process. [676] First, the seed surface can have imperfections, such as bubbles caused by the sintering process, which could cause defects in the device. Refinement of the sintering process should be able to overcome this challenge. Second, the severing technique used to separate the chip from the anchors needs to be optimized to improve yield, since currently there is a 5% loss of product due to this technique. Although this process is not yet ready for large scale manufacturing, it is on track to meet these challenges and provide a capability to produce flexible 3D-chips by 2020.

The technologies described in the previous paragraphs are just a few examples of new techniques that are being developed for the flexible electronics market. Since this field is still evolving rapidly, it is too soon to tell which process will be predominately used in the future, but it will most likely depend on the end application for the product of interest. Overall, these conventional electronics manufacturing methods, along with other methods that have yet to be discovered, will have to continuously adapt to the ever-evolving FHE industry.

4.3 Manufacturing Challenges for FHE

There are many manufacturing challenges that need to be overcome before roll-to-roll manufacturing of printed electronics becomes a viable production option. One hurdle to overcome is the development of standards for the industry, such as limits for surface roughness

and defects on a substrate. Defining standards and establishing libraries of standard components is crucial to the effectiveness of the roll-to-roll printed industry. [8] Once standards are developed, metrology techniques can become more focused, which will ultimately lead to better process control. [684] Additionally, having existing standards will assist the transition of a product from R&D to large scale manufacturing.

Not only do the "nuts and bolts" manufacturing issues need to be resolved, but bigger picture issues need to be addressed as well, as mentioned at the 2015 Flexible and Printed Electronics Conference in Monterey, CA. Investment money not only needs to be used for the R&D phase, but monies need to be allocated for scale-up, pilot production, and large scale manufacturing, as depicted in Figure 35. The pilot phase and volume manufacturing scale up tend to have the largest costs, but often a majority of the money is spend in the R&D phase, leaving nothing left to take the proven idea to market. In this case, the technology unfortunately sits in the lab while more money is sought from investors, risking that the idea will become obsolete in the meantime. Two companies that specialize solving these types of problems and taking FHE ideas to market are Soligie and Abbie Gregg Inc. In the end, how the various investment money is distributed will play a large role in whether an idea makes it to market.

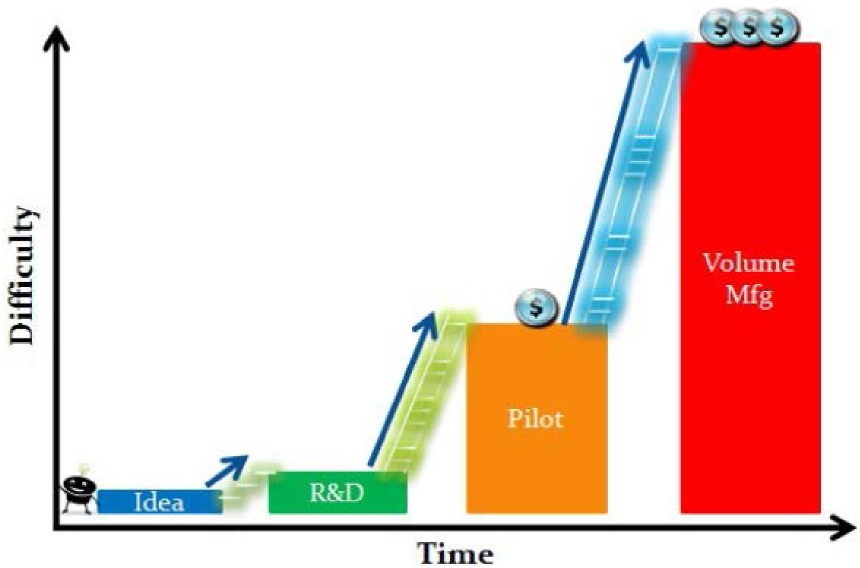


Figure 35. Transition from Research through Manufacturing [683]

Another manufacturing issue relates to the actual production of a product. After a technology is proven and foundries have been proven capable of producing a product, the production still needs to be scheduled. Unfortunately, because there are so few foundries that produce FHE, wait times for FHE can be several months at best. As more production facilities are established, this problem can be alleviated, but trusted foundry status will also be an issue. More and more production is being performed offshore, and many U.S. companies are being purchased by foreign entities, as was the case when Global Foundries, owned by the Emirate of Abu Dahbi, purchased IBM's electronics manufacturing division in July 2015. [685] Device logistics and device integrity may become issues as the FHE electronics market becomes increasingly global.

TECHNOLOGY GAP: MANUFACTURING TECHNOLOGY FOR FLEXIBLE HYBRID ELECTRONICS

Currently, there is a significant amount of investor funding being spent in laboratory phases of research without sufficient consideration or planning for scale-up and mass manufacturing processes.

POTENTIAL SOLUTION

Better planning and execution of research, development, and implementation for FHE is required, since scaling up from laboratory trials to pilot and large scale production often requires a large financial investment.

TECHNOLOGY GAP: MANUFACTURING TECHNOLOGY FOR FLEXIBLE HYBRID ELECTRONICS

A technology gap exists in the amount of research and development being conducted for metrology and process control methods for the FHE industry. These processes are what will drive manufacturing refinement and eventually reduce production costs and product variability.

POTENTIAL SOLUTION

Metrology and process control methods need to become more integrated, and the creation and adoption of standards will help to promote the improvement of these methods. Unfortunately, the adoption of standards could necessitate large investments in the form of equipment, which is why an organization like the FHE Manufacturing Innovation Institute is needed to lead this effort.

TECHNOLOGY GAP: MANUFACTURING TECHNOLOGY FOR FLEXIBLE HYBRID ELECTRONICS

Unfortunately, most manufacturing approaches to large area electronics are being designed to include stand-alone systems in conjunction with more standard fab technologies to complete a manufacturing line, which leads to loses in production efficiency.

POTENTIAL SOLUTION

More emphasis and effort needs to be placed on designing and engineering novel, integrated, manufacturing solutions in order to decrease the loses in efficiency.

TECHNOLOGY GAP: MANUFACTURING TECHNOLOGY FOR FLEXIBLE HYBRID ELECTRONICS

Due to cost competitiveness, many production facilities are moving overseas, or foreign entities are acquiring domestic electronics companies, causing a gap in trusted foundries and domestic capabilities for FHE manufacturing.

POTENTIAL SOLUTION

With the establishment of the FHE Manufacturing Innovation Institute, increased research and development by U.S.-based companies and universities will hopefully lead to an increase in the domestic capabilities for FHE manufacturing.

5.0 PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

In a general sense, electronics packaging comprises those elements of an electronic component that house semiconductor devices and provide mechanical and electrical connections between these devices and the electronic assembly or system where the component is used. In current electronics design and manufacturing practice, packaging can be "considered upstream or in conjunction with fabrication of [electronic] devices". [686]

The functions of an electronic package go beyond housing and interconnection. They include: (1) mechanical support for semiconductor devices; (2) physical housing to protect the devices from the environment; (3) sufficient means for removing heat generated by the semiconductor devices; and (4) electrical interconnections to allow signal and power flow to and from the devices to other elements in the electronic system. A well-designed electronic packaging solution must perform these functions while also satisfying design requirements related to system performance, reliability, manufacturability, testability, and serviceability; and constraints that include size, shape (form factors), weight, and cost. In general, these functions, requirements, and constraints do not change when considering FHE systems instead of conventional, rigid electronic systems. However, because of the emergent nature of FHE, packaging implementations for FHE are still rapidly evolving, and mechanical flexibility of electronic devices and substrates can present more freedom and more alternatives to product and manufacturing process designers. This gained freedom may come at the cost of additional uncertainty when moving away from better-known packaging alternatives utilized in conventional electronics.

Conventional electronics packaging has traditionally been categorized into the hierarchy of packaging levels shown in Table 22. This hierarchy implicitly considers the integrated circuit (IC) (aka microchip or chip) as a basic element of an electronic system, and it assigns the level 0 designation to the packaging methods that integrate various electronics devices inside a chip. Level 1 packages chips into modules that are mounted onto boards by level 2 packaging. Level 3 connects boards to other boards, and so on. Recalling that FHE defines a variety of possible combinations of electronics technologies (flexible chips on flexible substrates, rigid chips on flexible substrates, etc.), it is easy to conclude that a hierarchy for FHE packaging can be obtained from that of Table 22 by realizing that chips can be replaced by organic electronic elements; and chips, modules, and boards can (but do not ALL have to) be mechanically flexible. This generalization, however, may still not cover the entire variety of design structures that an FHE system can utilize. A hierarchy such as that of Table 22 may be difficult to develop due to the large number of possible combinations of technology that may go into an FHE system.

Table 22. Hierarchy of Electronics Packaging (based on similar table from [9])

Level	Description
0	**Gate-to-gate interconnections on the chip** – Package different functions (e.g. processing, memory, logic, chip level interconnects, etc.) onto a semiconductor chip.
1	**Chip-to-module connections** – Assemble one or more chips into a single chip module (SCM) or multi-chip module (MCM) – Examples are leaded, pin grid array, leadless, or area array packages; hermetic or non-hermetic, ceramic or plastic, encapsulated or tape automated bonding packages.
2	**Printed Wiring Board (PWB)-level interconnections** – Assemble leaded or leadless Level 1 packages, capacitors, resistors, memory, logic, power supplies, etc., onto a back plane or motherboard; or assemble a number of smaller cards with specific functionalities onto a panel.
3	**Board-to-board interconnections** – Package motherboard back planes, daughter boards, baby boards.
4	**Connections between sub-assemblies** – Box-level packaging with connecting cables, storage devices, cabling, rack or box mounting, etc.
5	**Connections between systems** – E.g. connecting computer hosts to terminals, printers, and other peripherals.

The remainder of this section describes several distinct state-of-the-art packaging technologies currently available in the industry or currently being developed that are considered part of FHE. It deals first with flexible circuits, which can be considered the first flexible version of printed circuit boards (PCBs). Initially developed decades ago, flexible circuits have seen significant progress and represent the natural evolution that starts from rigid PCBs toward the still futuristic high-performance flexible semiconductors on flexible packaging. Flexible circuits are covered in some detail here because many of the packaging considerations used for flexible circuits are still relevant when the electronic devices themselves are flexible and/or are fabricated (e.g. printed) directly on the flexible film substrate.

5.1 Flexible Circuits (Flexible Circuit Boards – Rigid/Flex Packaging)

The concept of mechanically compliant electronic assemblies is not new, although mechanical compliance was for years limited to foil-mounted interconnection devices such as wires and in more recent years to flexible circuit boards onto which passive and active electronic components are placed. These so called flexible circuits have been in the market since the 1950's, when they were initially developed to address requirements of the space program. "In its simplest form, a flexible circuit is a pattern of conductors printed on a flexible dielectric (insulating) film". [687]

In addition to enabling ranges of motion which are required in certain applications, flexible circuits can provide advantages in assembly time, weight, space, cost, and component density over their rigid PCB counterparts. Figure 36 compares two implementations of the same functional module for an unmanned air vehicle (UAV) application. Flexible or rigid/flexible implementations can often reduce SWaP requirements, be more reliable in shock and vibration environments, and provide good chemical and thermal resistance. As connective devices, flexible circuits have the following benefits with respect to traditional cabling and rigid boards: (1)

reduced wiring errors; (2) elimination of mechanical connectors; (3) design versatility; (4) higher circuit density; (5) wider range of operating temperatures; (6) improved signal to noise ratio and impedance control; (7) improved reliability; and (8) reduced size and weight requirements.

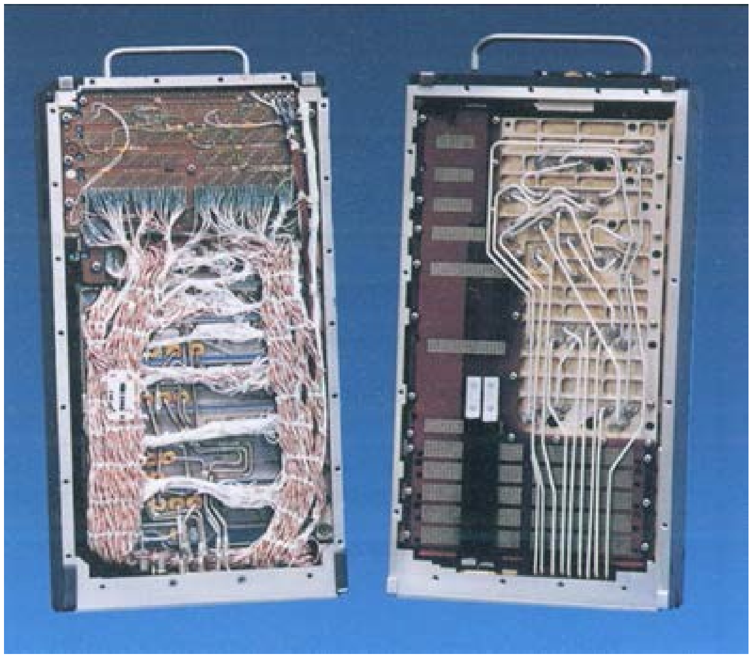


Figure 36. Flex / Rigid Flex PWB (right) versus traditional wire harness (left) packaging and interconnections (from Teledyne [688])

Table 23 defines terms that are useful for describing various flexible circuit options that are currently in the market. Clearly, these circuit implementations address neither mechanical compliance of (organic or inorganic) semiconductor devices, but they do represent a successful technology within the electronics industry and a definite step toward full mechanical compliance of electronic packages.

Table 23. Definitions for Flexible Circuits [686]

Term	Description
Flexible Printed Circuit	A patterned arrangement of printed circuitry and components that utilizes a flexible base material with or without a flexible (insulating) cover layer.
Rigid-Flex Printed Board	A printed board with both rigid and flexible base materials.

5.1.1. Materials and Manufacturing Implications of Flexible Circuits

A number of domestic companies provide flexible circuits for the aerospace, medical, industrial, defense, and communications industries. A sampling of these companies is provided in Table 24, with some of the product types that they supply. Each of these companies, and others that are not listed in the table, provides a selection of lines and spaces dimensions, vias dimensions, insulating materials (e.g. polyimide and DuPont PIC 1025), conductive materials, stiffeners, adhesives, plated finishes, and other specifications, all of which are crucial considerations for packaging of both conventional and flexible electronics.

Table 24. Sampling of Domestic Providers of Flexible Printed Circuits

Company	Examples of Provided Flexible Circuit Options
All Flex Flexible Circuits and Heaters; Northfield, MN	Flexible heaters; single- and double-sided flexible circuits; multi-layer flexible circuits http://www.allflexinc.com
Circuits, LLC; Murrysville, PA	Single-layer and double-sided flexible circuits; multi-layer flexible circuits; rigid-flex circuits http://circuits-corp.com
Circuits Unlimited, Inc.; Carson, CA	Single- and double-sided flexible circuits, with adhesive and adhesive-less base; multi-layer (up to 6 layers) flexible circuits; rigid-flex, adhesive-less materials only http://www.flexiblecircuitry.com
Epec Engineering Technologies; New Bedford, MA	Single- and double-sided flexible circuits; multi-layer flexible circuits; rigid-flex circuits http://www.epectec.com NOTE: In addition to its headquarters in Massachusetts and two other U.S. locations in Colorado and Florida, this company has facilities in China and the United Kingdom.
Flexible Circuit Technologies; Minneapolis, MN	Single-sided flexible circuits, with or without dual access; double- sided flexible circuits; multi-layer flexible circuits with/without air gap http://ww.flexiblecircuit.com NOTE: In addition to its headquarters in Minnesota, this company has two operations/facilities in China and one marketing office in Korea.
Flexible Circuits, Inc.; Warrington, PA	Type I , Type II , Type III, Type IV, IPC6013, MIL- P-50884 and IPC6012 Type I, II and III http://www.flexiblecircuits.net
Lenthor Engineering; Milpitas, CA	Single-sided through 30-layer flexible circuits; multi-layer rigid flex; staggered layer flex; dual side access; blind and buried vias; impedance control; book binder construction
Metrigraphics, LLC; Wilmington, MA	Flexible circuits, thin film devices, optical components, electroformed structures; use additive photolithographic processes, extreme resolution to manufacture microflex circuits with traces and spaces as small as five microns; products include single-layer and multi-layer flexible circuits, coils, sensor components, and electronics (e.g. for neuro-stimulation) http://www.metrigraphicsllc.com
Minco; Minneapolis, MN	High density interconnects (HDI) flexible circuits; rigid flexible circuits; multi-layer flexible circuits; double-sided flexible circuits; flex coils combining antenna coils and flexible or rigid-flexible circuits in a single rugged package; thin-film circuit manufacturing http://www.minco.com NOTE: In addition to its headquarters in Minnesota, this company has operations/facilities in France, Singapore, China, and Japan.
Teledyne Printed Circuit Technology; Hudson, NH	Single- and double-sided flexible circuits; multi-layer flexible circuits; multi-chip-module, chip-on-board, or surface mount packaging using rigid-flex substrates; high temperature (-55°C to 210°C) rigid / rigid-flex PWB and assemblies http://www.tetpct.com/ NOTE: Teledyne Printed Circuit Technology is part of Teledyne Technologies, a large company with operations primarily located in the United States, Canada, the United Kingdom, and Mexico.

5.1.2 Standards for Flexible Printed Boards and Printed Electronics

Single-sided, double-sided, multi-layer, and rigid-flex circuits are covered by standard IPC-6013, Qualification and Performance Specification for Flexible Printed Boards. Some of the listed companies have also manufactured to satisfy military specification MIL-P-50884, General

Specification for Printed Wiring Board, Flexible or Rigid-Flex (superseded for new designs after 1999 by MIL-PRF-31032, General Specification for Printed Circuit Board/Printed Wiring Board. In 2000, the IPC Flexible Circuits Committee issued a guide for Transitioning from MIL-P-50884C and MIL-PRF-31032 to IPC-6013 and AMENDMENT 1.

IPC has published three standards for printed electronics. The first two in 2012 and the last one in 2013:

1. IPC/JPCA-4921, Requirements for Printed Electronics Base Materials
2. IPC/JPCA-4591, Requirements for Printed Electronics Functional Conductive Materials
3. IPC/JPCA-2291, Design Guideline for Printed Electronics

IEEE maintains two standards related to organic electronics:

1. IEEE 1620-2008TM, Test Methods for the Characterization of Organic Transistors and Materials
2. IEEE 1620.1-2012TM, Standard for Test Methods for the Characterization of Organic Transistor-Based Ring Oscillators

No standard or design guide has yet been developed for packaging and/or integration of FHE. However, other standards are at various stages of development by IPC and other organizations for: (1) printed electronics test methods development and validation; (2) manufacturing (incoming bill of materials inspection, process control, and quality assurance); and (3) performance requirements for printed electronics assemblies. [689] These standards represent good steps toward a complete set of standards for FHE.

5.1.3 Advances in Flexible Circuit Technology

The flexible circuit market has continued to expand over the years, and the technology has seen many advances. Some of these advanced features are shown in Table 25, and many of them address packaging issues that are equally relevant for packaging of more advanced FHE cases.

Table 25. Advanced Features and Processes in Flexible Circuit Manufacturing

Advanced Flexible Circuit Packaging Feature	Description and/or Example
Air gap	Cases where layers are selectively bonded so that unbonded layers are allowed to flex more freely
Assembled components	Flexible circuits with assembled (active and passive) components (e.g. ICs, passives, membrane switches)
Controlled impedance	Necessary for higher frequency switching; accomplished, for example, by minimizing electrical reflections and ensuring error free transition between conductive tracks and interconnectors
Crimped pins	Mechanically attached to a circuit to allow for soldered connections
Graphic overlays	E.g. on membrane switches that may be lit by LEDs
Laser skived slots holes	Instead of manually created, for accurate manufacturing and assembly
Over-molding	For embedding electronic circuitry within the cable
Panelization	The stiffening of boundaries for ease of pick and place and wave soldering
Pressure sensitive adhesives	For easy assembly
Sculptured flexible circuits	With metallic conductors that vary in depth and thickness with respect to position to provide more strength at interconnection points
Shielding	E.g., solid or patterned aluminum foil electromagnetic shielding to reduce electrical noise and control impedance
Stiffeners	Applied in areas such as component assembly points or exposed traces to be plugged in for connection, both of which require additional support
Wire assembly connections	For cases where attaching conventional wiring is part of the best solution
Flexible heaters	Thin, bendable heating elements, where required
Ultrasonic welding	High frequency ultrasonic acoustic vibrations to build assemblies that are too small, too complex, or too delicate for more common welding techniques
Reliability for Dynamic Motion Applications	Single- or double-side flexible circuits for devices that require only a few hundred cycles over their lifetime (e.g. a hinged panel that opens only for maintenance or calibration) of for high cycle applications (e.g. a robotic arm that may require millions of repetitive motion cycles)

5.2 From Flexible Circuits to Flexible Hybrid Electronics Packaging

As previously mentioned, the packaging considerations for flexible circuits are still relevant in today's evolving world of FHE, and the evolution of this flexible circuit technology can be seen as a stepping stone from conventional packaging to the completely flexible semiconductors and electronics packaging envisioned through FHE. The previous sections have clearly demonstrated the highly integrated and multidisciplinary nature of packaging for flexible circuits, and they have stressed the importance of taking into account all of the various factors that are associated with this technology, including the materials, manufacturing processes, design guidelines, standards, etc. For example, one cannot adequately analyze electronics packaging without considering the adhesives used to attach individual components to substrates, the processes used to add/remove various layers of packaging materials, the variety of options for designing the package to module interconnects (pin grid array, ball grid array, surface mounting versus through hole, etc.), and the different sets of necessary standards depending on the specific application. Just as these areas drive packaging for flexible circuits, these same areas, in addition to others,

will also need to be considered for packaging technology for FHE and other innovative electronics technology in the future.

5.3 Hybrid Packaging of FleXTM Silicon-On-Polymer and Flexible Printed Electronics

American Semiconductor (www.americansemi.com) has developed the proprietary FleX process to transform standard silicon wafers into flexible wafers. [690] The process starts with CMOS chips fabricated using standard silicon on insulator (SOI) processes on 200mm wafers. The silicon is then removed and replaced with a polymer film to create ultra-thin (less than 200nm thick) SOI flexible wafers that can be diced into individual, fully functional FleX ICs. The resulting flexible (inorganic semiconductor) electronic devices are orders of magnitude faster than their printed (organic) counterparts. The packaging of these high performance FleX ICs in combination with flexible printed (passive and active) electronic devices can result in FHE systems that deliver the best of both technologies.

In American Semiconductor's Conformal Load-bearing Antenna Structures (CLAS) approach, flexible printed electronics deliver large form factor antenna elements, wiring, interconnects, and sensors, while the FleX SOI devices deliver CMOS-level performance in a flexible form factor that is compatible with the printed electronics. [690] In fact, high volume production of these FHE systems has been conceptualized as utilizing a roll-to-roll process where conductors, insulators, simple displays, power supply devices, and organic semiconductor devices are fabricated by various printing-plus-curing stages followed by attachment of FleX devices from a reel.

One possible disadvantage of the FleX technology is that since it is produced by standard fabrication methods, the time from order to delivery can be long, and the initial investment for setting up a manufacturing capability can be very large. That disadvantage is expected to be overcome by the industry having sufficient numbers of thinned IC wafers already produced to satisfy the expected demand for frequently used ICs (e.g., analog-to-digital converters and processing units) over time. Organic semiconductor devices, on the other hand, can be manufactured rapidly and at much lower costs, but will often not have the performance required by the application. The decision of what technology to use depends on performance, SWaP requirements, cost, delivery time, and reliability considerations, as should be expected.

5.3.1. Integration of Disparate Electronics Fabrication Technologies into FHE

The term Direct Write (DW) refers to the "selective deposition and patterning of material", and it is "capable of single- and multi-layer, high-resolution, material deposition on both flat and conformal surfaces." It is possible to integrate DW and printed electronics with rigid CMOS devices or flexible silicon-on-polymer devices. The result is an FHE device or system with the high performance characteristics of CMOS technology and the rapid production and versatility of DW and/or printed electronics. Packaging and integration are key areas for development and improvement for enabling pervasive applications and success of FHE, especially for military applications.

There are other related challenges that can at times be overlooked. First, the supply chains for different electronic technologies often have fundamentally different delivery times. FlexTM devices, for example, are manufactured, at least currently, from conventional electronics (batch)

foundry processes, and therefore can take significant time to be delivered, as mentioned in the previous sub-section. On the other hand, manufacturing of printed electronic devices and systems can be more much responsive with respect to delivery time, but obviously their performance is not comparable with that of thinned silicon wafers.

A second challenge is related to maintenance of FHE in applications. In essence, the component removal and replacement approach often used for repairing damaged conventional (rigid) electronics systems must be modified when dealing with damaged FHE systems. For example, removing and replacing FlexTM, organic electronics, and related systems that are printed or otherwise applied to aircraft surfaces is not currently as simple a task as the corresponding disconnect-unfasten-replace-fasten-reconnect processes often employed in maintenance of conventional electronic systems in field or depot environments. Substantial technology R&D and new standards are still required for establishing appropriate methods for maintenance of aircraft FHE systems. Design and manufacturing for maintainability must be a consideration before FHE can find widespread use in high performance systems for aerospace applications.

5.4 Introduction to Flexible Hybrid Electronics Packaging Criteria

Electronic packaging serves to isolate delicate electronics and system components from the environment in which they will operate, while appropriately connecting them to electronic assemblies for them to operate as required. Multiple, sometimes conflicting, considerations are required in the design process for a new component, and it is the responsibility of the designer to optimize these competing criteria. For example, conventional packaging for a component housed near a jet turbine will require high refractory materials that can withstand heat generated by the engine, resist attack from corrosive chemicals, and absorb near constant vibration experienced during multiple flights. These specifications must also be considered for the design of FHE packaging. However, unlike conventional packaging, FHE packaging must also be able to withstand repeated bending, torsion, and shear loads without compromising the performance of the electronic system. Furthermore, there is increasing demand for FHE to become more economical without sacrificing performance. A common approach to achieving this flexibility is to make the electronic system very thin (< 1 mm), though this creates additional challenges from fabricating components at such a small scale. In the next few sections, various packaging technologies in development and/or currently available today are discussed, in addition to the different criteria required for the application spaces these technologies fall within. A description of sources and vendors for materials and processes is also included, where applicable.

5.4.1 Packaging Criteria

There is no blanket set of performance criteria that can be applied to all levels of FHE or conventional electronics packaging. Rather, the specific requirements for an individual application and level of packaging hierarchy must be prioritized to ensure selection of optimal materials for the given operating environment. Common parameters that are considered include the extent to which the package is exposed to moisture, vibration, harsh chemicals, extreme heat, and mechanical stress including bending and torsion, among others. Additional considerations include cost, manufacturability, and availability of raw materials. Because these considerations can sometimes have competing requirements, it is essential to have a thorough understanding of the operating conditions that the package will experience. There are multiple commercially available materials selection software packages to expedite the selection process. These include

open source databases such as the Materials Section and Analysis Tool (MSAT) compiled by NASA and MatWeb, a spinoff of Automation Creations. Software packages, such as CES Selector by Granta, are also available for purchase and can offer the user a more streamlined and guided search experience, which can be especially useful for designers that are less experienced in materials selection procedures. An example of the materials selection process applied to an Air Force specific application is outlined below.

5.4.2 Packaging Materials Selection

To provide an illustration of the materials selection process, the following paragraph will consider the performance metrics for personnel monitoring sensors embedded into flight suits. These sensors must be mechanically robust to the withstand torsion, bending, and abrasion resulting from the pilot's movement. This eliminates ceramics and thermoset polymers including epoxies. The sensors must also be impermeable to moisture to prevent damage during frequent laundering and in the event that the pilot must make an emergency ejection into a body of water. This dictates that a moisture barrier coating, such as alumina or Parylene, be applied, though Parylene may be the better option due to its greater resistance to damage from scratching and extreme bending. To maintain vital sign monitoring in the event of an emergency, the sensors should also be able to withstand the extreme heat of a fire and attack from corrosive chemicals such as jet fuel. Polymers such as Teflon and poly(ethylene terephthalate) (PET) offer the greatest chemical resistance and temperature stability while maintaining reasonable flexibility and mechanical robustness. However, they tend to be much more expensive than other polymers and ceramics, though are also readily available commercially so material shortages should not restrict production. As this illustration shows, there is rarely a material that perfectly meets all of the specifications for a given application. It is, therefore, ultimately up to the component designer to optimize the trade-offs between these considerations and select the material that best meets the application requirements.

5.5 Packaging Interconnects

Previously summarized in Table 22 is a standard interconnection hierarchy of electronics packaging. This hierarchy is commonly used in conventional electronics to describe the different stages of the packaging, but can easily be adapted to outline the levels of packaging in an FHE system. Level 0 begins with the basic formulation of a (thin) chip and describes the interconnections between the gates and passives of a chip. Packaging scale continues to increase in subsequent levels, with chip to board interconnections (Level 1), interconnections on the board (Level 2), electrical connection between boards (Level 3), and finally connections between systems (Level 4/5). This packaging hierarchy is further explained as follows, including a description of how it can be adapted to FHE.

5.5.1 Level 0 – Gate-to-Gate Interconnections on Chip

This base level of packaging, Level 0, is actually a fabrication step that produces the devices or components that are to be packaged. For example, in order to package a complementary metal-oxide semiconductor (CMOS) device, one would first have to fabricate the CMOS device. In this case, Level 0 packaging creates the gate-to-gate interconnections on the surface of the CMOS die. These fabrication and design considerations occur at the wafer processing level and form the building blocks of the devices that are packaged using the technologies and processes described

in subsequent sections. One important goal of packaging, in general, is protecting these gate-to-gate interconnections so that they continue to function during use of the final product.

5.5.2 Level 1 – Connecting Chips/Passives to Board

Level 1 packaging focuses on assembling one or more chips into modules and preparing the modules for their end service environment. This may involve hermetic sealing for underwater or high moisture environments, or ceramic shielding for high temperature applications. In addition to these conventional design parameters, additional considerations are required when the modules must be incorporated into a FHE system, such as ultra-thin (< 50 µm) conformal and wearable electronics. Researchers at Auburn University [691] have identified two key techniques for chip to board connections in these systems: 1) thinned die flip chip bonded onto polyimide or liquid crystal polymer (LCP) films; and 2) thinned silicon die embedded in polyimide. The following sections discuss these two techniques in detail and provide a comparison to conventional bonding methods.

5.5.2.1 Flexible Flip-Chip Assembly

The two dominant flip-chip methodologies in the conventional packaging space are conductive adhesive bonding (isotropic or anisotropic), and solder bump (thermosonic or eutectic) bonding. Isotropic conductive adhesives conduct equally well in all directions, which means they can only be used between the appropriate metal contacts - those between which electrical conduction is desired. [692] In contrast, anisotropically conductive adhesives (ACA), are composite films in which a low-volume loading of conductive filler is incorporated into a polymeric adhesive. The low filler loading is essential to ensure that these films conduct in the very thin Z-axis, but do not conduct in X-Y axis. [693] These ACA films are also known as anisotropically conductive adhesive films (ACAF), anisotropically conductive films (ACF), or "Z-axis adhesives". A schematic of the use of ACA is shown in Figure 37.

The use of ACA in flexible flip-chip bonding was explored, in 2000, by researchers with the 3M Company and the Microelectronics Research Laboratory in Columbia, MD. [694] For this experiment, a 50 µm thinned silicon memory chip was used. In order to raise the pads above the 8 µm polyimide passivation layer, gold stud-bumps were bonded to the pads. However, the gold stud-bump was 25µm high, and so it reached 17 µm above the passivation layer. The researchers suggested using an alternative electroless nickel-gold bumping process to create bumps only 5µm above the passivation surface, which would reduce stress on the flexible chip. An experimental 3M ACA was used between the bumped chip and the substrate, and a 15 lb. force (250 psi) was used to bond. Several chips fractured at this force during testing, showing a need for further process development.

Improving upon this technology, a Telephus Inc. research group, in 2004, developed a multilayered ACA to improve the wetting properties of the resin on two-layer flex for better interface adhesion and to increase the reliability of the interconnection under thermocompression bonding. [695] The multilayered ACF showed better adhesion properties and stronger moisture resistance than the single-layered ACF.

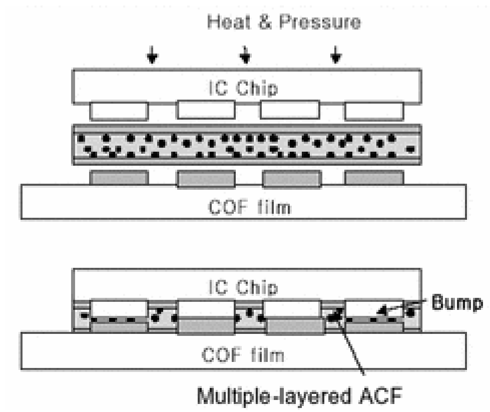


Figure 37. Chip-on-Film Flip Chip Bonding Procedure [695]

A gentler process for flip chip bonding of flexible chips using eutectic Sn/Pb solder bumps was devised at Auburn University in 2008 [696], and is shown in Figure 38, with a final assembly shown in Figure 39. The procedure was tested with a 10mm x 10mm daisy chain silicon chip with 1368 Sn/Pb solder bumps on a 250 µm pitch. Interconnects on the surface were established by processing a layer of polyimide onto the silicon, followed by a layer of chrome/copper interconnects, and finally a layer of polyimide with windows for connection pads etched.

Flexible substrates were manufactured from a copper-clad polyimide laminate (DuPont Pyrolux AP). Each silicon die thinned down to 30 µm was attached to a temporary handle die to make it manageable for processing, and then wafers were bumped to create Sn/Pb solder bumps on each die pad. A vacuum fixture constructed from a porous sintered block of stainless steel was used to stabilize the flex substrate during the placement, reflow, underfill dispensing, and curing stages of flip chip bonding. The solder bumps were reflowed in a nitrogen environment oven at 230 °C. After overnight dehydration to drive out solvents, underfill was dispensed to fill the space between the chip and substrate, and then cured. One key disadvantage of solder-based flip chip assembly relative to adhesive-based is the time required for dispensing and capillary flow of underfill resin, which is seen as incompatible with volume manufacturing. [697]

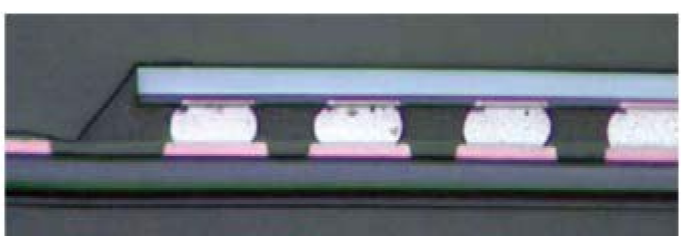


Figure 38. 50-µm-thick Die Flip Chip Bonded with Sn/Pb Solder Bumps

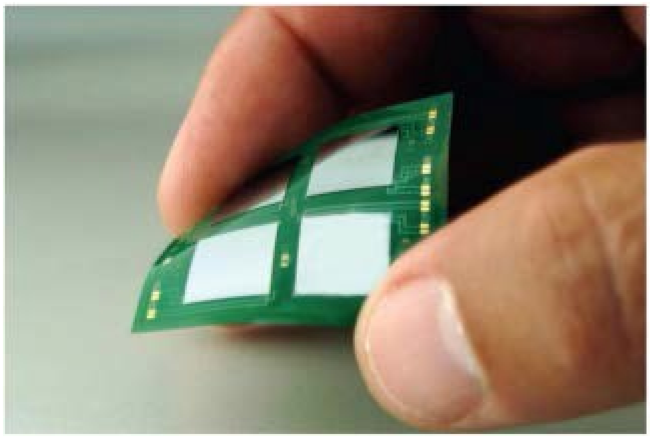


Figure 39. Flexible Flip-Chip Assembly [696]

The Fraunhofer Institute for Reliability and Microintegration and the Technical University of Berlin conducted reliability investigations, in 2006, into both ACF and solder reflow flip-chip-on-flex technologies. [698] In thermal ageing, both technologies showed very high reliability. Cu/Sn soldered modules showed first failures after 2500h in 150 °C, and ACF samples showed no failure after 3500 hours in 125 °C. Both technologies showed low reliability in temperature/humidity testing (85°C/85%RH) with a failure rate of 30% after 300 hours. The presence of humidity and temperature seriously affects the interconnections of both technologies, and so moisture barriers and encapsulations become critical for these technologies.

5.5.2.2 Polyimide Embedded Interposers

As the pitch on chip-scale packages becomes finer, the tolerance demands for various processes likewise become tighter. While assembly bonding may need to place a bumped chip in the appropriate location with less than a few hundred microns of precision, at the entire assembly level, copper traces may be printed with millimeters of precision. One solution to this challenging, wide range of specifications is the use of an intermediate structure that allows a transition from a tight tolerance to a wider one. A visual representation of this structure is a fan-out board, or breakout board, where small pitches fan out to more easily accessible ones, as in Figure 41. At the microelectronics level, this mechanism for interfacing a small pitch chip and a larger tolerance substrate is known as an interposer.

The combined efforts of the Centre for Microsystems Technology (CMST) of Ghent University and Imec (Belgium) in 2011 yielded an embedded ultra-thin chip package (UTCP) in a flexible circuit board. This collaboration is ongoing and seeks to develop miniaturized systems with small chip packages towards small, lightweight, comfortable (if it is for wearables), and conformable systems in medical, sporting, consumer, and industry application spaces. [699] An overview of the process is shown in Figure 40.

The process uses off-the-shelf obtainable dies and a variety of processes to thin the Si dies down to 15-35 µm. Many of these processes are in Section 4.2, and include developments such as FleX™ Silicon-on-Polymer™ by American Semiconductor, ChipFilm™ developed at the Institute for Microelectronics in Stuttgart, back grinding, and others.

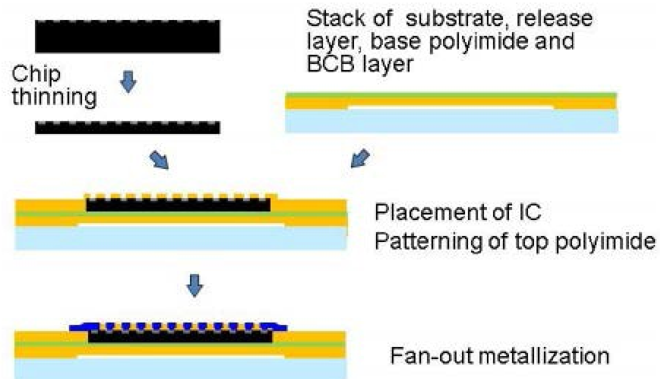


Figure 40. UTCP Embedding with Flexible Interposer [700]

After thinning, a rigid carrier is coated with a 400 nm release layer of evaporated potassium chloride (KCl) salt and photo-patternable polyimide, such as HD4110 (Hitachi-DuPont). Benzocyclobutane (BCB, Cyclotene 3022-46 from Dow) is applied and cured to attach the thinned dies to the substrate. A second layer of HD4110 polyimide is then spun and patterned to remove the polyimide on the surface of the contact pads. At this point, the entire chip is embedded in 16-40 µm of polyimide, with openings at the contact metalizations. Copper traces, 6 µm thick, are sputtered, electroplated, and patterned to create the fan-out of the flexible interposer. The package is then released from the substrate, and the KCl release layer is dissolved in water [10]. The resulting flexible interposer is shown in Figure 41.

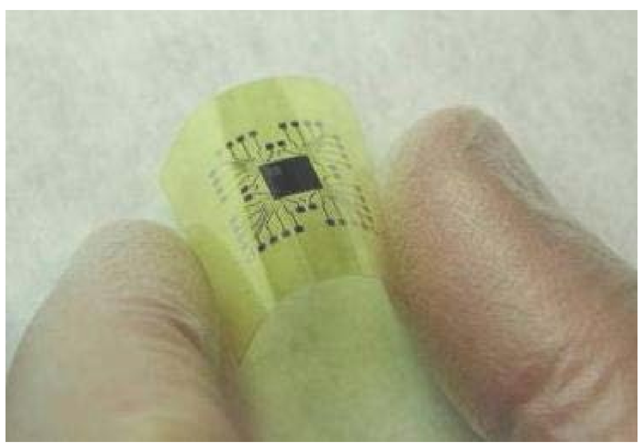


Figure 41. Flexible Embedded Ultra-Thin Chip Package Interposer [699]

A somewhat newer (2012) process from CMST and Imec includes extra steps to produce a “chip cavity”, reducing the step height that copper traces must cross from polyimide to chip and spreading pressure distribution on the chip to prevent cracking. [699] This newer process also includes backside illumination of the substrate after the chip is adhered to the substrate and photo-patternable polyimide is spun, which removes any polyimide on the surface of the embedded chip, but leaves polyimide at the same height as the chip. Finally, a third layer of polyimide is spun, and patterning for metallization occurs again.

The Fraunhofer Institute for Reliability and Microintegration (IZM) extended this interposer technology, in 2010, to yield ultrathin three-dimensional interposer stacks, combining ACAs and flip chip technology. [701] Each interposer consists of three layers of polyimide with electroplated Au vias between two-level metallization of sputtered Au, and has 10-12 µm thinned dies flip chip bonded onto the interposer. The flip chip assembly thickness is limited to < 20-50 µm, utilizing ultra-thin chips (< 20 µm). Prototypes assembled by Fraunhofer IZM included 4 flip chip levels with a total thickness of 170 µm. Figure 42 shows the stack and assembly method. A stacking sequence of 1) interposers, 4) flip chips with 7) interconnects, and 5) ACA layers including 6) conductive particles is shown. The interposers are double sided substrates with 2) metal layers on both sides, 8) vias, and 3) at least one internal wiring layer.

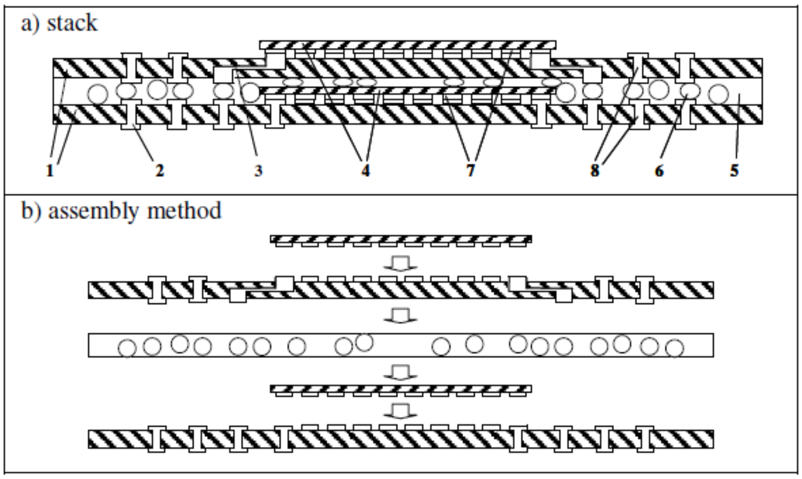


Figure 42. 3D ACA Flexible Interposer [701]

5.5.3. Level 2 & 3 - Interconnections between Chips and Passives, Board to Board

Level 2 in the hierarchy of conventional packaging describes PWB-level connections - that is, the traces and connection structures that create electrical connection between various components on a board, such as passives and chips. However, in FHE packaging, the dividing lines between Level 1 and Level 2 packaging can become blurred because the processes and steps that provide interconnections between various chips (Level 2) are the very processes on which the chips are connected to the board or flexible substrate (Level 1). In this section, Systems-in-Foil embedding will be discussed, followed by an overview of the different methodologies for forming flexible or stretchable interconnections.

5.5.3.1. Systems-in-Foil Chip Embedding

Systems-in-foil (SiF) are a class of flexible electronic products where complete systems are integrated into thin, polymeric foils. [702] These systems may be integrated in hybrid flexible electronics where the substrate must have sufficient flexibility to conform to the shape of a rigid housing or body, or in wearable electronics where the device experiences frequent bending. While fully functional polymer integrated circuits have been demonstrated, the performance of such devices is not comparable to silicon or other III-V materials, and so embedding flexible, ultra-thin devices is necessary. By thinning chips and using miniaturized or flexible components, the overall thickness of a SiF can be less than 100 µm. Each of the previously discussed packaging technologies is used to fabricate these systems. In addition, concepts such as

multilayer foil embedding can be expanded to encompass the various system-level connections involved in Level 2 packaging. Table 26 shows some commonly used polymer substrates.

Table 26. Properties of Common Polymer Substrates [703]

Material	Max. Deposition Temp. (°C)	Properties
Polyimide (Kapton)	250	Orange color; high thermal expansion coefficient; good chemical resistance; expensive; high moisture absorption
Polyetheretherketone (PEEK)	240	Amber; good chemical resistance; expensive; low moisture absorption
Polyethersulphone (PES)	190	Clear; good dimensional stability; poor solvent resistance; expensive; moderate moisture absorption
Polyetherimide (PEI)	180	Strong; brittle; hazy color; expensive
Polyethylene Napthalate (PEN)	160	Clear; moderate CTE; good chemical resistance; inexpensive; moderate moisture absorption
Polyethylene terephthalate (PET)	120	Clear; moderate CTE; good chemical resistance; inexpensive; moderate moisture absorption

The Holst Centre and Imec have described a low-cost, roll-to-roll compatible 2011 process for embedding chips in foil to produce packages only 60 µm thick. [704] These systems are commonly realized with copper traces on polyimide, but the Holst Centre focused its efforts, in 2011, on low-cost substrates such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) with silver or copper interconnections. These polyesters pose significant challenges due to their narrow operating temperature range. All processing steps for PEN must be performed below 180°C, and PET must be performed below 150°C.

The process flow begins with a single copper foil, which also serves as the interconnection for the system. At this point, either an isotropically or anisotropically conductive adhesive is dispensed to serve as a die attach. If isotropic adhesive is used, care must be taken to precisely dispense the adhesive where it is needed for the contacts of a die, and a non-conductive adhesive must then be dispensed in between those conducting bumps. ACA works well in ultrafine-pitch applications, in combination with Au/Ni bumps on the die. The actual embedding of the chips occurs in a lamination step using PET film and a suitable adhesive. The adhesive flows around and encapsulates the embedded chips, and so void-free lamination is crucial. Typical dimensions of this embedding morphology are chip thicknesses of 30 µm, a 20 µm die bond adhesive layer, and a 50µm thick PET film. An adhesive thickness of 70 µm to 100 µm will therefore result in an overall thickness of less than 200 µm. This work from the Holst Centre, shown in Figure 43, resulted in ten out of eighteen good electrical connections. Further study into improving the reliability of these processes is necessary.

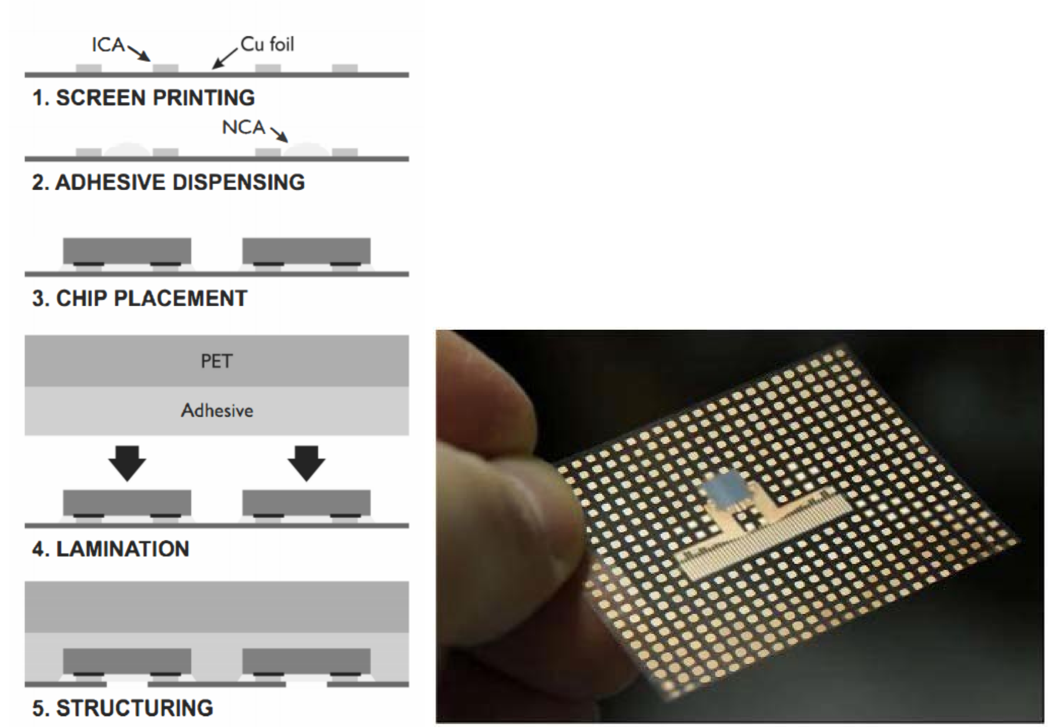


Figure 43. System-in-Foil Embedding Approach by the Holst Centre [704]

As manufacturers seek to increase component density on increasingly smaller chips, layout of the necessary copper traces between the chip components becomes more difficult due to limited real estate. This is because the copper traces must be patterned such that they make the required electrical connections between the desired components without touching other traces, which would render the design ineffective. To resolve these technical limitations, Imec with the Holst Centre adapted the single-layer technology discussed above to a double-layer chip embedding technology in 2012. The process, as illustrated in Figure 44, embeds circuit components in a core layer of thermoplastic polyurethane (TPU) film, which is then sandwiched between two layers of copper foil from which traces are formed. [705] Copper via holes are bored through the PET to provide conductivity between traces on either side of the PET film, when needed. Either ICA or ACA is used to attach the components to the copper foil. These components can be thinned die or a number of passives. One of the key benefits of the double-layer embedding is the ability to embed passives, resulting in a completely flat encapsulated device. A thermoplastic polyurethane (TPU) film, such as the Epurex Platilon U2102, is selected as the encapsulating host material. A 100 µm TPU film is placed between the copper foil with the chips and another copper foil and laminated for 5 minutes at 160 °C and 5 bar or for 2 minutes at 170 °C and 7 bar. Via holes are then drilled through the TPU substrate and filled with an electrically conductive paste. Via drilling is performed using a CO2 laser, sometimes followed by a KrF excimer laser for cleaning. The appropriate material properties and performance criteria for the via-filling conductive paste are the subject of active investigation by the Holst Centre.

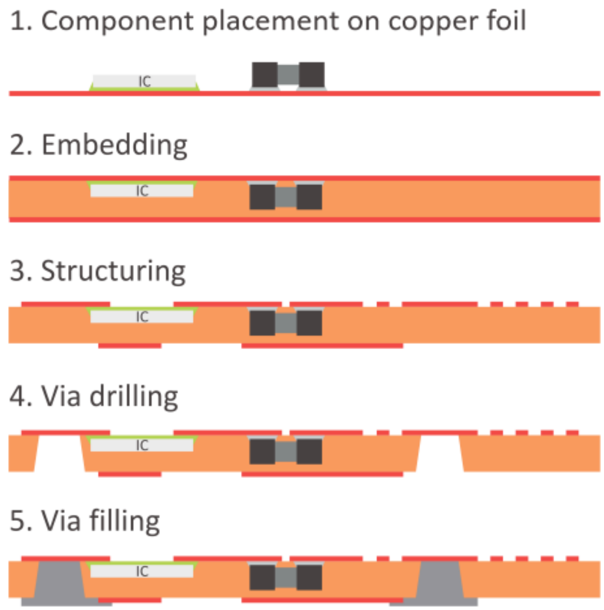


Figure 44. Double-Layer Embedding in Systems-in-Foil Technology [705]

5.5.3.2. Flexible / Stretchable Interconnects

The concept of flexible interconnections is not a particularly new one. The original "flexible circuits" concept is one that is prevalent in applications where two rigid objects must move relative to each other and have electrical connection between them, whether this is performed using rigid substrates with flexible interconnects or using an entirely flexible board and interconnects.

For example, a polyimide-based ribbon cable moves along with a printer head as it rasters over a page. These copper flex interconnect assemblies in the ribbon cable are well-established and manufactured by numerous companies, who often have capability for manufacturing flexible printed circuit boards as well. In addition, flat flexible cables (FFCs) have been established as the flexible parallel conductor and interconnect of choice in many hardware systems. These may be obtained off-the-shelf in pitches down to 0.5 mm and thicknesses down to 0.3 mm. A sampling of companies providing these resources is shown in Table 27.

Table 27. Commercial Suppliers of Copper Flex Interconnects and FFC

Company	Technology / Examples of Flexible Interconnect Options
Molex / DuPont	DuPont Pyralux TK substrate, Rigid flex, high speed flex assemblies, flex backplanes, high density flex jumpers, flex interconnect assemblies, flexible power connections, single, double, multi-layer (up to 18+ layers), through-hole, SMT, BGA, press-fit [707, 708] http://www.molex.com/
Meritec	Flex Interconnect Termination System (FITS), Liquid Crystal Polymer substrate; right angle, vertical board edge, and cable to cable mount; 10-20 contacts, U.S.-operated / ITAR capable [709] http://meritec.com/
Flex Interconnect Technologies	18+ layers, integration with flexible circuits, high speed flex connector cables, interconnections for flex, rigid-flex, and high- density interconnects (HDI), Mil-P-50884, ITAR compliant http://www.fit4flex.com/
Parlex, Inc. (Johnson Electric)	0.50 mm to 2.54 mm pitch with 1-99 conductors, commercial-off- the-shelf parts, LIF and ZIF connectors. http://www.parlex.com/

Printable inks can also be used on flexible substrates to form conductive traces and act as flexible interconnects. These inks and the processes used to deposit them are discussed extensively in Section 3.0 and Section 4.0.

One of the most intriguing areas of development in flexible hybrid electronics is stretchable interconnects. Flexible interconnects and printed circuits allow electronics to bend and conform to a variety of surface structures without being plastically deformed. In this sense, flexible electronics are able to conform to cylindrical or even conical geometries, but only a stretchable electronics structure is able to conform to a spherical geometry. Highly conformable electronics are essential for wearable or implantable electronics. These stretchable interconnects can form the basis for a deformable "hybrid" electronic system, where rigid or flexible components are placed on islands within a stretchable substrate (Figure 45), and the geometry or physical characteristics of interconnects are selected to allow them to stretch with the underlying substrate. Thin metal films are found to fracture under a tensile strain of ~1% [710], but conformal electronics may require cyclic elongation and relaxation of 15% or more.

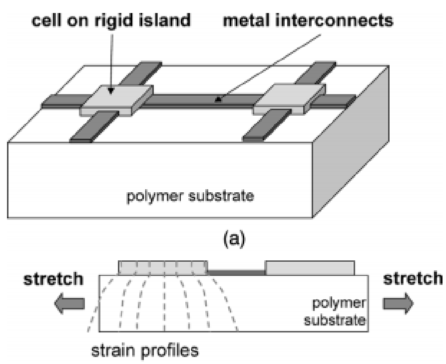


Figure 45. Example of Stretchable Electronics Design [711]

One way of achieving this increased toughness in the metal interconnects is to "pre-stretch" copper traces to create wavy geometries capable of being stretched, which has been studied by a group at Princeton University, in 2005. [711] As shown in Figure 46, a 1-mm-thick PDMS membrane (Sylgard 184 from Dow Corning) is used as the substrate, and is uniaxially pre-stretched by 10%-25%. Metal film conductors are e-beam evaporated onto the stretched substrate with thick photoresist used as a shadow mask for the conductors. Upon release, the conductors form waves, allowing stretching of approximately 12%, and compression of over 25%.

Unfortunately, this mechanical pre-stretching is incompatible with most coplanar processes, due to the added complexity of uniformly stretching the material and maintaining stretch throughout the fabrication process. Figure 46 depicts the (a) as-prepared PDMS substrate, (b) prestretched PDMS, (c) laminated riston photoresist mask, (d) evaporated metal films, (e) lift-off, and (f) release.

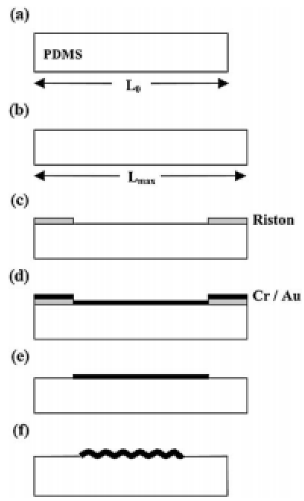


Figure 46. Fabrication of Gold Interconnects on Elastomeric PDMS Substrate [712]

Another method to realize stretchable interconnects is to create serpentine geometries that allow the planar structure to twist out of plane. Serpentine metal interconnects can sustain over 200 cycles of elongation by 25%. [713] This technology acts like a spring when stretching, and generally is a Cu conductor patterned in the shape of a repeating horse-shoe. Imec developed, in 2011, a stretchable horseshoe-shape metal conductor, shown in Figure 47 [714], which is embedded in polyimide and has high resistance to fatigue and excellent strain performance**.** The polyimide-embedded conductor is embedded in a flexible substrate, such as PDMS. This circuit topology was determined to have an ultimate elongation of 250%, and a reliability of 40,000 cycles at 30% elongation.

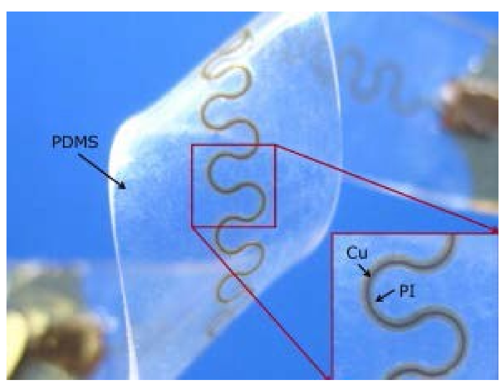


Figure 47. Stretchable Polyimide-Embedded Interconnect [714]

A team at the King Abdullah University of Science and Technology (KAUST) demonstrated, in 2014, a stretchable conductor topology capable of up to 800% elongation, integrated into an adhesive skin patch for thermotherapy. [715] In this work, shown schematically in Figure 48, rigid islands of thermoelectric heating pads were connected using a double horseshoe spring structure without any underlying substrate. The metal spring interconnects served as both electrical connection and structural framework. Fabrication occurred on a silicon wafer, during which each spring was encased in polyimide for additional protection, then the integrated spring and heating pad was released from the silicon wafer through XeF2 etching.

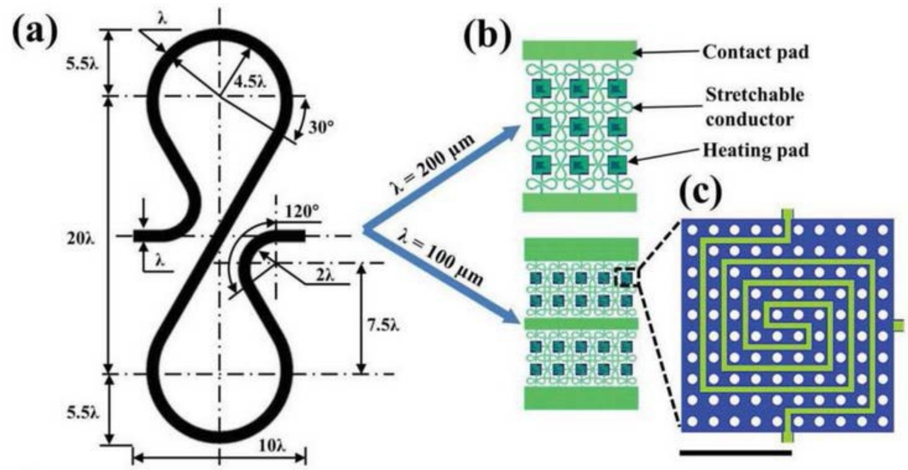


Figure 48. KAUST Stretchable Interconnect [705, 715]

The 800% maximum elongation caused plastic deformation, and so the springs were further evaluated to be able to return to their original state after 100 cycles of stretching up to 600%. Researchers at KAUST have also developed an "ultra-stretchable monolithic silicon fabric", shown in Figure 49, composed of islands of silicon wafers with highly stretchable spiral springs as electrical and mechanical interconnects. [716] Such a construct can be considered to be a MEMS device, but it is fully CMOS-process compatible. The combination of hexagonal silicon island and a single 5 μm spiral were initially 1.1m with a final stretched length of ~11.5m. The spiral springs are cable of expanding up to 1000%, corresponding to a system stretch of 50% and resulting in a stretched fabric area of 2.25 times larger than the resting area.

Figure 49. "Ultra-Stretchable Monolithic Silicon Fabric" [716]

5.5.4. Level 4 & 5 – Connections between Sub-Assemblies & Systems

In general, interconnections between sub-assemblies and systems are already flexible in nature, and take the form of cables and wires. In this way, the interconnections of FHE systems do not vary widely from those of convention electronics.

Novel approaches to level 4 & 5 interconnections in FHE are predominantly wireless connections. Wireless technology allows for flexible electronics with built in antennas to connect

and communicate with personal devices, such as phones, hot spots, and wireless routers, or to serve tactical purposes for radar communication or electronic warfare. In this scenario, the dividing lines between levels are blurred again. Mechanically, the formation of the antenna occurs in “Level 2”, in that the metallization for such an antenna would be fabricated along with other board-level interconnects, but the antenna provides its function at Level 4 & 5; through these antennas, system-level and inter-system communication is available.

The dominating market for flexible antennas lies in radio-frequency identification (RFID) devices. In pursuit of the Internet of Things, where “things” are embedded with electronics, software, sensors, and network connectivity for collecting and exchanging data, the development of flexible antennas for Bluetooth or wireless connectivity is essential.

A team at the University of Arkansas has investigated the design, fabrication, and testing of flexible antennas, fabricating them on a Kapton polyimide substrate using ink-jet technology. Of course, any of the previously discussed metallization schemes (evaporation, sputtering, etc.) can be used, but ink-jet printing is an extremely versatile, roll-to-roll capable process. The flexible antenna devised is shown in Figure 50. Conventional microstrip antennas are not practical for flexible electronics due to their dependence on the substrate’s thickness; there, a novel flexible Planar Inverted-F Antenna (PIFA) design, not unlike that used widely in mobile phones, was implemented. It was designed from the ISM 2.45 GHz band, one of the most commonly used bands, where WLAN, IEEE 802.11/WiFi, Bluetooth, PAN, and ZigBee operate. The team has also explored textile antennas, paper-based antennas, fluidic antennas, and flexible bow-tie antennas.

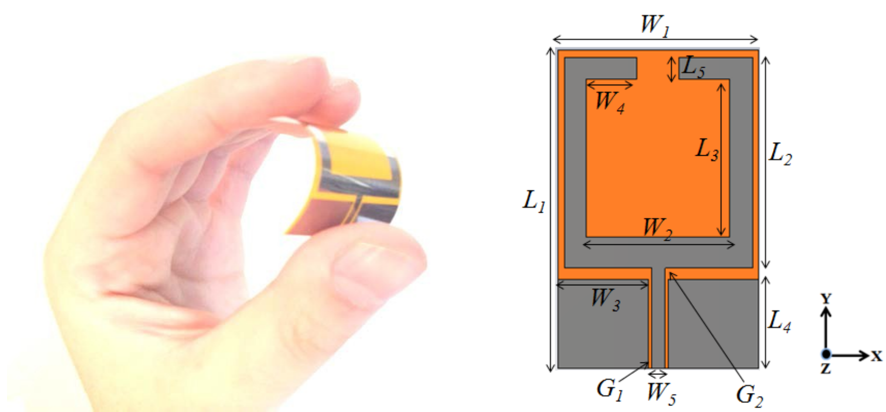


Figure 50. Flexible Antenna Structure on Polyimide [717]

The University of Sheffield and the Stretchable Bioelectronics Group at the University of Cambridge, in England, have devised a PIFA antenna evaporated on PDMS capable of operating under 10% strain, with completely reversible deformation. [718] The technology used to yield a 100 nm stretchable gold conductive layer is discussed in Section 5.5.3.2. However, this design showed 10 dB loss compared to an antenna fabricated on FR4 (a common glass-reinforced epoxy laminate used for printed circuit boards), due to the thin metallization. The group continued their research by producing a stretchable dipole antenna, which was created by printing 400 nm thickness conducting silver inks onto pillar patterned PDMS substrates. This design gave only 1.7 dB of loss compared to FR4, but stretching was not completely reversible after 10% strain.

This dipole structure is illustrated in Figure 51. Further research into this type of flexible design is needed to yield an antenna with lower loss and reversible deformation. This form of antenna could conceivably be conformed to a variety of non-conducting surface topologies, and existing interconnection technologies – solderable SMA connectors, coaxial cable – can be used to supply a signal to it.

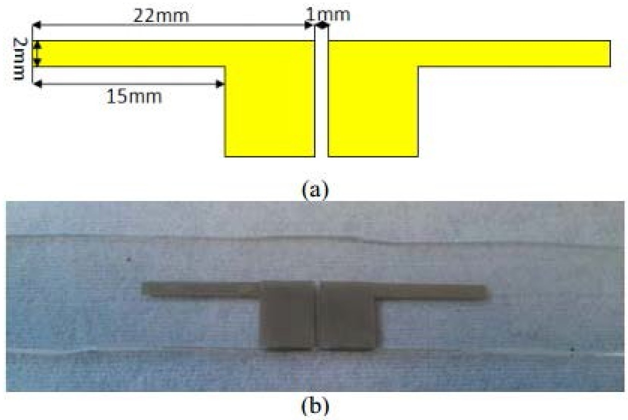


Figure 51. Printed Dipole Antenna

For a phased array antenna system, conformal arrays become difficult because the geometry is so drastically change under load. A Master's thesis defended, in 2012, at North Dakota State University and supported by DARPA describes a 2.47 GHz 1x4 printed array that includes sensing mechanisms to adjust the phase shifting to each individual array based on the strain on a resistive sensor. [719] The schematic of this layout is shown in Figure 52.

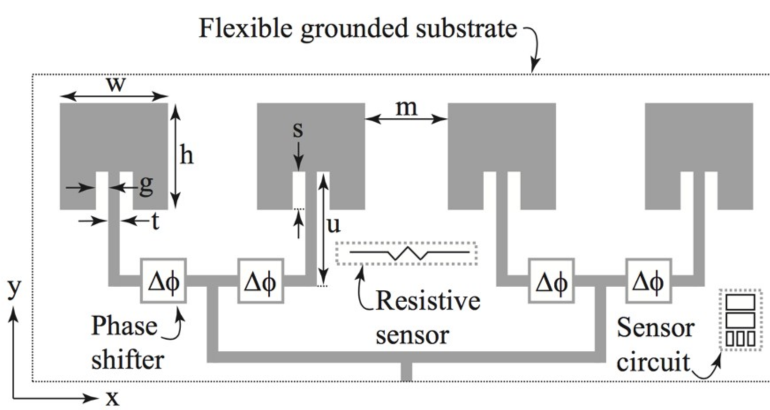


Figure 52. Conformal Phased Array Radar

Much research is required to develop this field of flexible, conformal antennas for aircraft, wearables, and other applications. Additional research in this area could generate a host of adaptive radar systems capable of responding to changes in their topological environment, as well as radar systems that can be placed in unique conformal locations.

5.6 Encapsulation

The components of flexible electronics, especially those composed of organic materials, are extremely sensitive to moisture and show degraded performance in humid environments. In addition, as discussed previously, metal interconnections suffer when exposed to humidity, and less than 1% moisture content present in multilayer packages can result in accelerated interfacial delamination. [719] It is therefore critical to establish encapsulation processes that will protect the electronics from moisture during all stages of operational life. While different materials exhibit a range of water permeability, no material can provide an environment completely devoid of water, so it is the challenge of packaging science to select materials that offer an acceptable moisture rejection for a given application space or requirement. Materials and methods must also be established to prevent the ingress of moisture at edges and seams.

Several other parameters are key in the selection of an encapsulating material. The material must exhibit good adhesion to the substrate to which the components to be protected are affixed; poor bonding between the encapsulant and substrate will cause delamination, which compromises the moisture blocking properties. The material must generally be electrically isolating to prevent shorting or damage to the underlying electronic components. In addition, extreme temperatures and exposure to harsh chemicals will require selection of encapsulants with wide operating temperature ranges and resistance to chemical attack. The thermal requirements of the end application must be considered to ensure the proper encapsulant is selected. Furthermore, flexible hybrid electronics have the unique requirement that every material must be able to undergo a certain amount of mechanical flexing without breaking, buckling, delaminating, or compromising any other properties that are required to meet the targeted performance.

The photovoltaics industry has established a wide set of encapsulant materials useful for moisture protection of inorganics. Superstrates – those on the surface of the solar cell – must obviously have certain optical transmittance properties, while substrates – the supporting material of the photovoltaic - must provide mechanical structure and support to the cell. Layers to mechanically protect the delicate electronics are generally added between the components and both the substrate and the superstrate, shown in Figure 53.

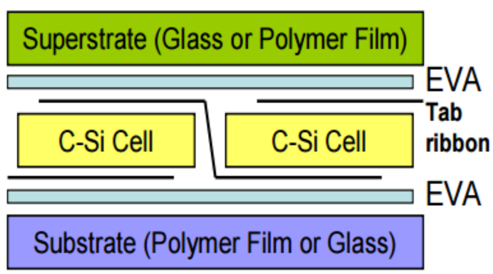


Figure 53. Typical Crystalline Si-based Photovoltaic Module Encapsulation Structure [720]

Ethylene-vinyl acetate (EVA) has been the nearly universal encapsulant of choice in the photovoltaic industry since the early 1980s. [721] Encapsulant materials development is an active area of research, and some of the most notable options currently available include thermoplastic polyurethane (TPU), polyvinyl butyral (PVB), silicones, ionomers, and other proprietary polymers. Properties for a few commercial encapsulant materials can be found in

Table 28; the water vapor transmission rates (WVTR) for polymeric films used as moisture barriers are typically reported in units of 100 - 102 g / m2-day.

Table 28. Commercially Available Encapsulation Films

Company/ Material	Type	Water Vapor Transmission Rate (WVTR) g / m2-day	Volume Resistivity (ohm-cm)
DuPont PV5400	Ionomer	1.7 (0.38mm)	6 x 1015
DuPont PV8600	Ionomer	0.84 (0.38mm)	7.1 x 1016
STR Photocap 15455P	EVA	18 (0.46mm)	>1 x 1014

As flexible electronics technology progresses, the moisture absorption rate tolerances become much tighter. For sensitive technologies such as OLEDs, the WVTR needed almost seven orders of magnitude higher than what organic polymers, such as EVA, TPU, or silicone, can provide. A spectrum of barrier technologies is shown in Figure 54.

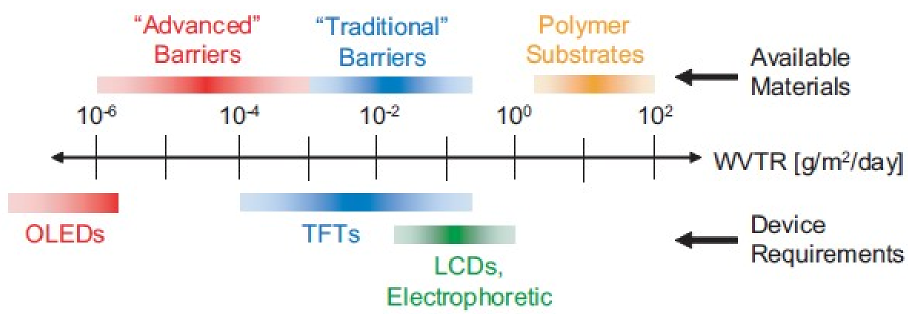


Figure 54. WVTR Requirements of Various Flexible Organic Technologies

One approach to the permeation problem is the use of thin-film permeation barriers, formed from Al or Si oxides. Bulk oxides and Al are effectively impermeable to oxygen and water, as are high purity SiO2 films. However, the presence of defects, nanoscale pores, or pinholes when the films are deposited via PECVD, sputtering, or evaporation can degrade oxygen transmission rates (OTR) and WVTR performance to only two or three orders of magnitude better than polymer thin films. In spite of this, concerted efforts to realize thin films with higher film density have resulted in single-layer films with WVTR rates of 8 x 10-5 g/m2-day. Researchers from the University of Colorado have reported Al2O3 films with a WVTR of 1 x 10-3 g/m2-day by utilizing low-temperature atomic layer deposition. Work at Lappeenranta University of Technology in Finland has resulted in the development of a high-throughput ALD process that reaches 5 x 10-6 g/m2-day, utilizing a "spatial ALD" concept to implement roll-to-roll deposition. SoLayTec, a Dutch company, has made available a commercial high-throughput spatial ALD system capable of processing up to 4800 wafers per hour, designed for solar cells. ALD layers of Al2O3 less than 10 nm thick show critical compressive and tensile strains of greater than 2%. [730]

For situations such as implantable objects, a biocompatible encapsulation material is necessary to protect the electronics from body tissue, corrosive body fluids, electrolytes, proteins, enzymes, and lipids, as well as protect the human body from the electronics. One such suitable encapsulation material is Parylene C, a coating applied by gas-phase polymerization to form a

thin, transparent film whose thickness may be controlled over several length scales. [730] Parylene has been demonstrated to be an extremely effective biocompatible encapsulant due to its high inertness and purity. Unfortunately, Parylene C as a permeation barrier suffers greatly from poor adhesion to metal, ceramic, and polymer substrates. [731] In order to remedy this, some sort of adhesion promoter is required.

Researchers at the Laboratory for Sensors at Albert-Ludwigs-University of Freiburg, in Germany, combined glow discharge polymerization and chemical vapor deposition of Parylene-C, in 2014, to form a permeation barrier with excellent adhesion properties. [732] Glow discharge is suitable for a wide range of materials and modifies surfaces to promote adhesion with modifications ranging from a simple cleaning of the surface to a generation of a very thin (nm range) layer of polymer. Magnetron enhanced glow discharge of trimethylsilane (TMS) at 15 kHz was used to make the surface of the target substrate more suitable for Parylene film. Then Parylene deposition occurred in the same vacuum chamber using the standard Gorham's process. The result was super adhesion due to the radical-radical bonding between Parylene and the plasma polymer generated during glow discharge polymerization.

Bi-layer encapsulation with ALD of Al2O3 and Parylene-C was studied at the University of Utah, in 2012. Plasma-assisted atomic layer deposition (PAALD) was used to establish 52 nm Al2O3 films using trimethylaluminum (TMA) gas as a precursor, upon which 6 µm of Parylene C were deposited using the standard Gorham process. Silane A-174 from Momentive Performance Materials was employed as an adhesion promotor between the Al2O3 and Parylene-C layers [11].

Multi-layer coatings of both organic and inorganic materials also form permeation barriers with good properties. The National Chung Hsing University [734]developed, in 2007, a multilayer Parylene, silicon nitride, and silicon oxide coating that achieved 2.5 x 10-7 g/m2-day WVTR initially, and 2.5 x 10-6 g/m2-day after 5000 cycles of flexing over a 2 cm diameter . The WVTR of a single bilayer stack of 50nm SiOx and 50 nm SiNx deposited by plasma-enhanced chemical vapor deposition (PECVD) was determined to be 2.1 x 10-3 g/m2-day, and the WVTR of a single tri-layer stack of 300 nm Parylene/50 nm SiOx/50 nm SiNx was determined to increase to 7 x 10-3 g/m2-day. By depositing several of these stacks, WVTR would improve, but would asymptotically approach a critical value due to lateral leakage through the edge of the stack. Further improvement was obtained through a preheating process to drive water absorbed during the deposition process out from the organic layers. A barrier structure SiNx/SiOx/Parylene/ SiNx/SiOx was chosen, and each sample was heated in a PECVD chamber at 20 mTorr for 30 minutes at an optimized temperature of 120°C to achieve a WVTR of 2.5 x 10-7 g/m2-day. One company that offers multilayer encapsulation technology is Vitriflex, who claims an all-inorganic barrier stack of polymer films, obtaining a WVTR down to 10-6 g/m2-day.

Novel permeation barriers are critical avenues of research in the coming years, including edge barrier technologies that minimize the lateral leakage on the edge of the encapsulation stack, thin-film coatings with better optical and permeation properties, and roll-to-roll implementations of a variety of common thin-film processes for materials such as Parylene, bulk oxide, and organic/inorganic stackups.

5.7 Present Challenges

Flexible hybrid electronics show promise as the next generation of innovative circuit technologies, but a flexible electronics device is only as reliable as the package it is placed in. These packages perform the dual functionality of providing electrical interconnections between layers of the packages and protecting the prime electronic functionality from damage by the environment in which it is placed.

Many of the technologies presented in the previous sections have potential for success, but have not yet been vetted for the reliability that is required for consumer or, especially, military applications. These immature technologies require devoted time spent establishing processes and reliability tests to truly determine the application spaces for each novel technology presented. In addition, very few of the methods presented have been adapted for large scale production or manufacturing integration, and it will require a concerted effort to prepare and equip industry to fabricate and package systems, with the aid of various research facilities around the country. It is important to note that the majority of the packaging technologies presented throughout these sections are being studied outside of the United States, particularly Germany with Fraunhofer IZM, Belgium at Ghent University and Imec, and King Abdullah University of Science and Technology (KAUST) in Saudi Arabia.

A summary of current technology gaps is presented in the boxes below.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

Current technology gaps for FHE packaging technologies, with regards to manufacturability, include yield, reproducibility, lifetime, and reliability metrics.

POTENTIAL SOLUTION

Increased research and development for manufacturability of FHE packaging technologies. Due to the importance of packaging as an enabler for FHE technologies, this topic will perhaps be addressed by the FHE Manufacturing Innovation Institute in the near future.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

Large-scale silicon wafer thinning procedures need to be developed in order to enable ultra-thin chips, as well as wafer and die handling processes to prevent curling of the chips.

POTENTIAL SOLUTION

Alternative technologies can perhaps be leveraged from American Semiconductor's FleX™ Silicon-on-Polymer process. Additionally, other materials besides silicon can be investigated for use in ultra-thin chips, including III-V, II-VI, CNT, nanowire, organics, and thin semiconducting film materials.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

A technology gap exists in the ability to mechanically support the electronics devices and components without hindering the electrical connections.

POTENTIAL SOLUTION

Development of novel embedding processes to simultaneously mechanically support embedded components and provide electrical interconnections, without fracturing any pieces of the device.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

A technology gap exists in the capability to create conformal electronics without the loss of any electrical performance.

POTENTIAL SOLUTION

Development of novel, flexible, stretchable interconnections and ruggedized flexible packages.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

Large scale deposition processes for encapsulation materials that provide protection from moisture and other elements while still maintaining acceptable optical transmittance.

POTENTIAL SOLUTION

Improved encapsulation materials need to be developed with novel permeation barriers that are efficient for both inorganic and organic materials. Additionally, development of roll-to-roll deposition processes for encapsulation materials is key for large scale manufacturing of flexible electronics packages.

TECHNOLOGY GAP: PACKAGING FOR FLEXIBLE HYBRID ELECTRONICS

An important challenge in FHE packaging technologies is the ability to integrate rigid and flexible materials and devices at high speeds.

POTENTIAL SOLUTION

Creative manufacturing methods will need to be developed in order to address this technology gap, and these creative methods could be further researched through the FHE Manufacturing Innovation Institute.

6.0 DESIGN TOOLS FOR FLEXIBLE HYBRID ELECTRONICS

The modern synthesis process for designing flexible hybrid electronic (FHE) assemblies is not fundamentally different from the design process for conventional rigid electronics. For most flexible hybrid circuits, the design process is performed with manual entry into the same computer Electronic Design Automation (EDA) tools used in conventional rigid designs. These EDA tools assist with schematic entry; layout of the flexible, rigid-flex, or hybrid circuit board; design rule checking; and simulation of the design. However, most modern commercially available toolsets do not explicitly cater to the design of flexible circuits. The design of EDA tools to support flexible electronics specifically is an open and active field of research. In the near future, tools to mechanically and electrically simulate boards across their complete freedom of motion will allow designers to produce better circuit performance and reliability, lower electromagnetic emissions, and decrease the length of the design timeline.

Currently, the design process for FHE is typically performed manually by the human designer. Looking forward, design automation of flexible electronic circuits will continue in a similar manner to what is seen in conventional circuits. Increases in computational power and algorithmic advances in the iterative feedback loop of design to simulation and back will continue to produce significant advances in automated tool design. Flexible electronic EDA tools of the future will allow for the seamless and automatic creation of electronic schematics and board layouts, blending rigid printed circuit boards (PCBs) with many different flexible substrates, producing accurate electrical and mechanical simulations of the design, and checking for satisfaction of all design requirements for manufacturing and test, all with minimal human design input.

The following sections will cover standards applicable to the FHE design industry along with in-depth discussion of current and future design tool trends for the design, test, and manufacturing of FHE.

6.1 Applicable Standards

Much like with conventional rigid electronics, IPC, the Association Connecting Electronics Industries, has achieved wide-spread acceptance throughout the electronics design industry and received ANSI development recognition for standards related to the design and manufacturing of flexible circuits.

Table 29 below lists some of the accepted IPC standards applicable to FHE design. It is not intended to be an exhaustive list; however, these standards are the typical high level specifications applicable to modern flex circuit design, test, and production.

Table 29. Applicable Industry Standards for Flexible Hybrid Electronics

IPC Standard Number	Standard Title	Current Revision Date
IPC-2221 [760]	Generic Standard on Printed Board Design	11/2012
IPC-2223 [761]	Sectional Design Standard for Flexible Printed Boards	11/2011
IPC-4101 [762]	Specification for Base Materials for Rigid and Multilayer Printed Boards	08/2015
IPC-4202[763]	Flexible Base Dielectrics for Use in Flexible Printed Circuitry	04/2010
IPC-4203[764]	Adhesive Coated Dielectric Films for Use as Cover Sheets for Flexible Printed Circuitry and Flexible Adhesive Bonding Films	01/2013
IPC-4204[765]	Flexible Metal-Clad Dielectrics for Use in Fabrication of Flexible Printed Circuitry	02/2014
IPC-6013 [766]	Qualification and Performance Specification for Flexible Printed Boards	12/2013
IPC-6202 [767]	Performance Guide Manual for Single and Double Sided Flexible Printed Wiring Boards	02/1999
IPC-FA-251 [768]	Assembly Guidelines for Single and Double Sided Flexible Printed Circuits	02/1992

IPC-2221 establishes design specifications covering high level electronics design principles applicable to a wide range of electronics, from conventional rigid systems to flex PCBs. It provides general requirements for circuit schematics, board layout, material selection, board mechanical properties, component placement, thermal management, process documentation, and quality assurance. For more detailed requirements, IPC-2221 references a hierarchical chain of standards that specifically cover design entry, rigid circuit board fabrication and assembly, and electrical component requirements. This standard has considerable influence on the entire process chain of conventional and flexible electronics design synthesis.

IPC-2223, much like IPC-2222 for conventional electronics, takes the requirements and specifications detailed in IPC-2221 and applies them more specifically to flexible PCB fabrication and assembly. This standard provides guidance for flex PCB design such as substrate adhesives and adhesive less material information, standards for connecting flexible PCB regions to rigid regions, mechanical considerations, as well as requirements for board layout, manufacturing, and quality assurance. IPC-2223 also defines five different classifications of flexible circuit board types. These board types cover simple single conductive layer flex circuits all the way to rigid/flex hybrids with multiple conductive layers, stiffeners, and plated through holes. Below in Figure 55 is an illustration of the five types of IPC-2223 class flex PCBs.

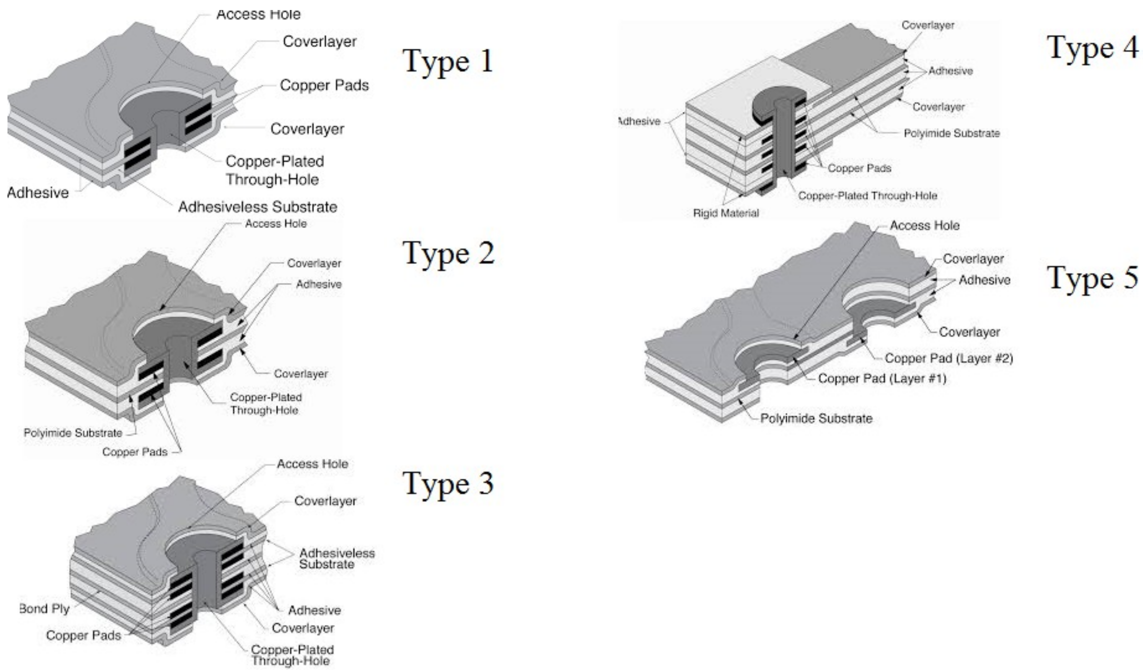


Figure 55. Illustration of IPC-2223 Board Types [761]

IPC-4101 covers classifications and requirements for laminates or prepreg used to fabricate both rigid and flexible circuit boards. From a design tools viewpoint, this standard offers guidance that flex circuit tools must take into consideration about laminate weight and thickness tolerances, mechanical peel strength, chemical properties such as flammability and solderability, and much more.

IPC-4202 is a corollary to IPC-4101, except for the use of non-conductive base dielectric layers instead of the laminate. This standard has specific designations and requirements for the common base dielectrics seen in modern flexible circuits such as polyvinylfluoride (PVF), polyethylene terephthalate polyester (PET), and polyamide-imide. Additionally, the standard contains requirements for base dielectric thickness, tensile and tear strength, permittivity, and chemical composition. Two very similar companion standards are IPC-4203 and IPC-4204. IPC-4203 is a similar standard covering the chemical, mechanical, and electrical properties of dielectric films used as cover sheets for flexible printed circuits, while IPC-4204 details metal-clad dielectrics.

IPC-6013 is the flexible circuit corollary to IPC-6012 for conventional rigid circuit boards. IPC-6013 standardizes fabrication and qualification of bare flexible printed circuit boards. Along with IPC-A-610, IPC-6013 details classes of electronics specified to determine the required level of testing, inspection, and documentation completed during fabrication, assembly, and acceptance testing of manufactured electronic systems. Most military electronic design is performed at Class 3 levels in both standards. This requires the highest level of post fabrication and assembly inspection, testing, and documentation and is intended to provide the highest level of quality and reliability. IPC-6013 is generally accepted by both commercial vendors and government agencies as equivalent to MIL-PRF-31032.

IPC-6202 and IPC-FA-251 are performance and testing requirements performed on flexible circuit assemblies. Unlike IPC-6013, which only details requirements for bare flexible printed circuit boards, IPC-6202 and IPC-FA-251 detail the manufacturing and testing required for the completed assemblies (boards with parts mounted). These standards focus on manufacturing issues such as cracks, bowing or twisting of the assembly, part placement registration, residue from adhesives or solder used during assembly, and mechanical/electrical/environmental testing post-assembly.

6.2 Conventional Design Tools

The fundamental design flow for flexible electronic circuit boards closely resembles that of conventional rigid electronics. Circuit schematics entry, part selection and placement, and conductive layer routing all occur in much the same manner and with the same tools. The major design difference between conventional rigid and flexible circuit boards is accounting during circuit board layout for the mechanical flexibility of the substrate to move, bend, or flex once produced. Because of this freedom of motion in flexible substrates, flex circuits usually have looser tolerances for spacing of physical circuit features such as mounted parts, through hole vias, electrical traces, or mounting holes. [769] The circuit designer and EDA tools must account for these tolerance differences through the use of special design rule areas in mixed rigid/flex designs or changing project-wide rules in flexible only designs.

During printed circuit board (PCB) layout, the circuit designer manually enters a flexible stack-up layer design into the layout tool. This stack-up layer explicitly informs the EDA tool of the number and type of conductive, dielectric, and cover layers present in the flexible or rigid-flex regions of the design. For areas where parts will be placed, stiffener locations can be input into the stack-up as well. Figure 56 below represents an example PCB stack-up with multiple flexible conductive layers, an added stiffener, and dielectric cover overlays.

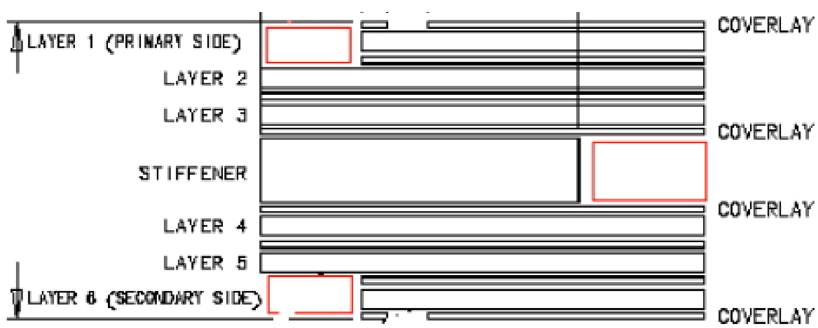


Figure 56. Example Stack-Up for Rigid Flex Circuit Card [770]

Multiple different layer stack-ups can also be setup across varying regions of the designed PCB, as demonstrated in Figure 57. This allows for the creation of PCB regions with stiffeners, regions without stiffeners, regions where the numbers of conductive layers differ to improve flexibility, and rigid areas all on the same design. [771]

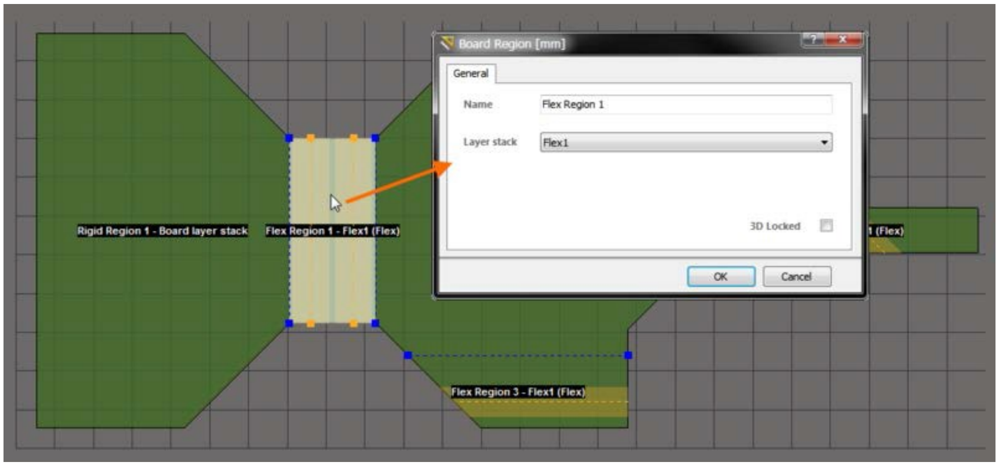


Figure 57. Multiple Layer Stack-Up Regions in Altium Designer [771]

Once the circuit designer enters the stack-up into the EDA tool, special keep-out areas for parts, signal traces, or through-holes that cannot bend or have limited flexibility are then entered into the design. The designer can then add additional design rules such as requiring trace arcs perpendicular to the expected bend lines, strain relief fillets at endpoints, or increased trace width in flexible regions to ensure reliable electrical connectivity across the entire specified bend radius. From this point, layout can continue similarly to a conventional design with automated or tool assisted routing.

The trend towards computer automation of conventional rigid circuits is also seen in modern EDA tools. Flexible board layout tools of the future should be able to programmatically define optimal layer stack-ups, select appropriate copper routing rules in flex regions, and incorporate electrical and mechanical simulation feedback to produce high performance and robust designs across many different types of laminate, flexible or not.

6.3 Simulation Tools for Mechanical Flexibility

One of the major differences between conventional rigid electronics and flexible hybrids is the increased range of bending, flexing, and twisting motion to which an assembled flexible hybrid circuit is subjected to during its lifetime. Circuit board flexibility can impact part and board feature placement on a design's substrate in a manner that is difficult to visualize using traditional 2D computer EDA toolsets. As such, modern mechanical computer aided design (MCAD) tools allow designers of flexible circuit boards to simulate in 3D the effects of a design's expected full range of motion on mechanical stability, reliability, and performance. [772]

By importing a board outline, substrate types (such as polyimide), substrate thickness, layer stack-up, bend axes, maximum bend radii, and part placements from their standard design tools into the mechanical simulation tool, a designer can manipulate a board in all directions of specified movement. Using the 3D model, the designer can then investigate potential issues, such as board and part clearances, enclosure fitting, mechanical stabilization of mounted parts, tear relief, and copper trace stretching. [772] Figure 58 shows an example 3D visualization of a bend simulation performed in the Altium design and simulation suite which through MCAD

modeling found a potential clearance issue between mounted LED parts and a flexible region of a rigid-flex circuit board.

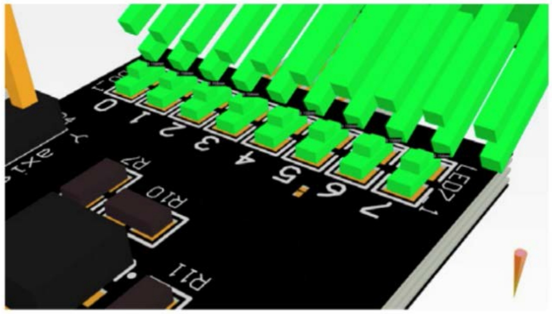


Figure 58. Simulated Bending of a Flexible PCB in Altium Designer [773]

MCAD tools can also help highlight potential issues with the use of rigid components on flexible laminate. Mechanical EDA tools, such as Solidworks Simulation, are beginning to incorporate finite element (FE) simulation algorithms to help simulate board fatigue and failure scenarios under inflexible components so that designers can take proactive steps during the initial design phase to increase board reliability. [774] By simulating areas of the board that are subject to high levels of mechanical stress, potential failure scenarios and the impact of design solutions, such as strain relief and board stiffeners, can be investigated to help prevent failures post-manufacturing. Such tools also often incorporate thermal simulation in addition to mechanical bending to better model the impact of heat deformation on the flexible substrate and mounted parts. [775] For example, in Figure 59, an FE simulation of thermal and mechanical stress on a flexible substrate highlights a potential design issue, where a part mounted on flexible polyimide is potentially subject to bending beyond allowable specification.

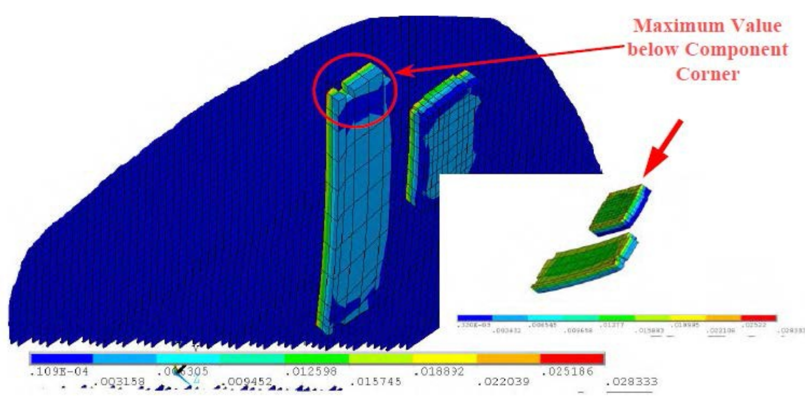


Figure 59. Simulated Thermal and Mechanical Stress on a Flexible Substrate [775]

As EDA tools for both rigid and flexible circuits become highly automated, the feedback of design rule failures and simulated errors into the automated place and route toolset becomes increasingly useful. Smart MCAD tools of the future will use design specifications for board size, bendability, operational environment, and mounted parts to layout and simulate optimal

board layer stack-up, part placement, copper routing, and mechanical strain relief, all with minimal input from a human designer.

6.4 Simulation Tools for Electrical Properties

As much as circuit board flexibility impacts mechanical design considerations, a flexible circuit board's freedom of movement affects the electrical performance characteristics of a designed flexible hybrid circuit. As a board bends and flexes, the spacing between conductive metal is altered, creating the potential for complex electromagnetic interference and radiation. Additionally, the dielectric performance of flexible laminates such as polyimide can differ substantially from traditional rigid laminates such as FR4. [776] These issues unique to flexible hybrid circuits can significantly impact design features such as antenna gain, matched impedance traces, transmission line performance, and electromagnetic compatibility through increased spurious EM emissions. As such, modern EDA electrical simulation tools are developed to model EM performance across a defined range of circuit mobile flexibility, construction materials, and copper feature placement. [777]

To perform electromagnetic modeling, a circuit designer exports the relevant design features such as physical size and shape, laminate/adhesive/cover layer types, copper layout/thickness, layer stack-up, part placement locations, and flexible regions from the board layout and MCAD tools into an EDA simulation environment. The designer can then use an electrical simulation tool, such as Mentor Graphics' Hyperlynx, to define a range of allowed motion along specified axes. Such tools then use simulation algorithms, such as finite element analysis (FEA) or full wave electromagnetic simulation, along with the design's electrical constraints to simulate signal integrity and EM interactions between board components during discrete steps of the bending motion. [778]

Using the simulation output, board designers can visualize any electrical design issues that may exist, such as increased spurious EMI emissions in specific flexible orientations or signal integrity loss due to impedance mismatches as the distance between conductive traces change. Then, in an iterative approach, corrective layout or board changes can be made before once again simulating; this process can be repeated until acceptable performance is achieved.

Also much like mechanical simulation, the need for automated electrical design simulation and feedback with the place and route layout EDA tools increases as the entire toolchain becomes more automated. Currently, any feedback from simulation toolsets is handled manually by the circuit designer though implementing improvements and iteratively testing and modifying the design. Another current limitation is that the freedom of motion is limited to predefined paths in bending zones. However, future EDA chains could incorporate automated design manipulation techniques like evolutionary design through both electrical and mechanical simulation to further remove the human from the design loop. It is also reasonable to expect mechanical and electrical simulation tools of the future to converge and co-simulate mechanical stress along with electrical behavior. That convergence combined with increased range of motion in all axes rather than solely along predefined bending zones will increase the simulation accuracy in future designs.

6.5 Embedding Components in Flexible Substrates

A consistent trend in electronics design is increased functionality in ever shrinking physical size. This has rapidly caused packaging density of electronic components and wiring to increase while available space to mount the top or bottom side components decreases. To increase the available area for placing components, integrated module board (IMB) technology has been under research and commercial development for the past 15 years allowing the implantation of rigid active components inside of a rigid or flexible substrate. [779] Embedded wafer-level packaging (EWLP), chip in polymer (CIP), and embedded chip build up (ECBU) technologies are more recent research developments allowing the more flexible and size efficient silicon wafers of electrical components to be used. [780]

For FHE, the embedding of the more flexible silicon die or ultra-thin chip package (UTCP) without its rigid and rugged packaging, allows for increased flexibility of designs by reducing the need for stiffeners or rigid laminates around the packaged components. The surrounding flexible laminate provides protection of the die and direct routing of copper traces to the die's pads. The reduction in size that embedded components offer make it ideal for high speed components due to the reduced electrical patristics in shortened trace lengths between components. [779] In Figure 60, a microcontroller UTCP is shown embedded in the flexible substrate of a circuit board demonstrating the potential for increased flexibility compared to surface mounted rigid components.

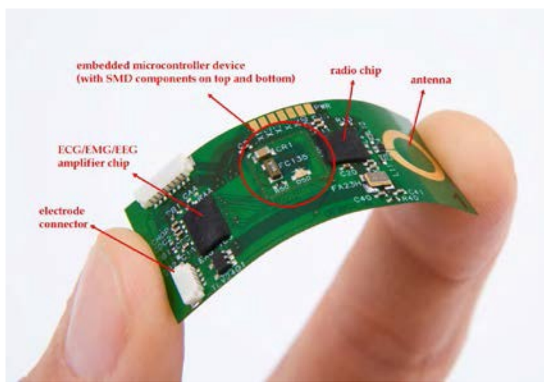


Figure 60. Microcontroller Die Embedded in Flexible Substrate [781]

To enable designers to embed components in modern designs, modern EDA layout and part placement tools such as Altium Designer and Mentor PADS suite are beginning to natively support active and passive component embedding into cavities or embedded regions of laminates. The design flow is manually intensive, requiring designers to actively select regions in a board's layout (as seen in the example below) to have a modified layer stack-up and routing rules. Once the embedded region is defined in the layer stack-up, electrical connections can then be routed to electrical interconnects on the die or UTCP component. [781] This information is then conveyed to manufacturing in the IPC-2581 or another common (ODB++) data format so that components can be included during board etching and lamination rather than part assembly. [771]

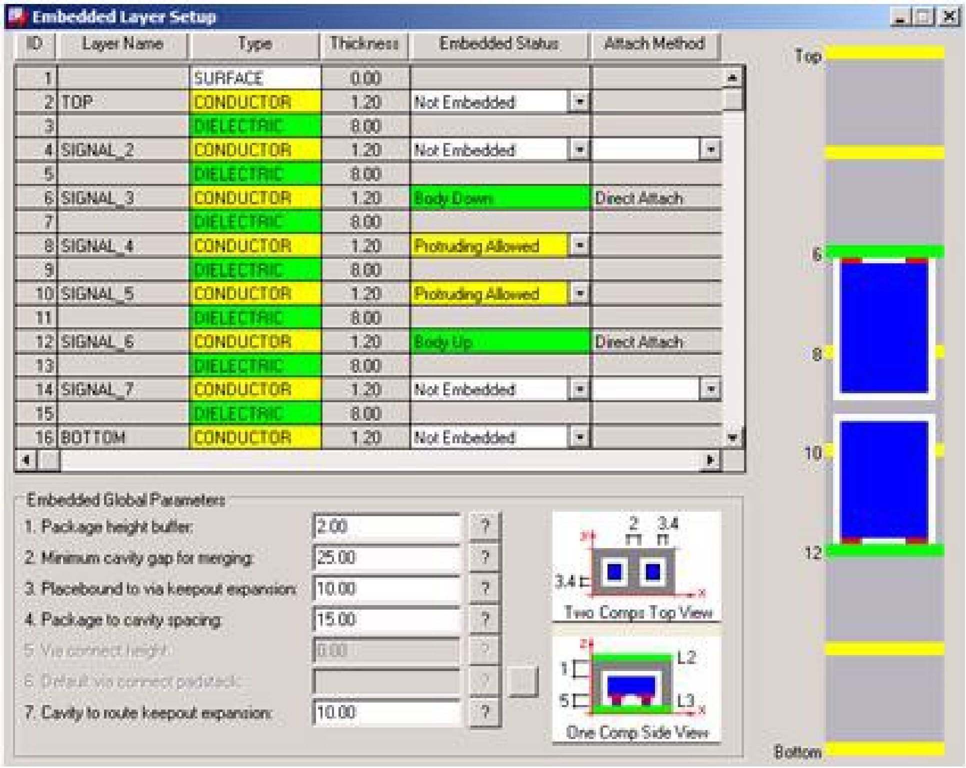


Figure 61. Allegro Layer Stack-Up for Embedded Components [782]

In the near term future, decreasing the manual nature of this process and allowing easy automated design time decision for embedding components should be expected. Components that are available in embeddable wafers or packages can be selected by the designer who will then leave the placement, stack-up modification, and routing to EDA place and route tools. In the long term, integration with mechanical and electrical simulation tools need further funding and research to push commercialization. Components embedded between layers of silicon and metal shielding will obviously behave differently with regards to electrical, mechanical, and thermal performance. Current simulation tools are generally unable to properly simulate this type of packaging and board design at a robust level. As seen in other areas, full automation of placement and routing embedded components should be expected in the long term future as simulation tools and evolutionary development algorithms begin to surpass human design capability.

6.6 Tools for Printed Conductors on Textiles or Plastic, Glass, and Paper Laminates

Using flexible laminates, such as polyimides or PVF substrates, allows circuit designers to follow many of the same design conventions and use EDA tools in much the same manner as when using FR4 or other traditional rigid laminates. However, the integration of electrical components and wiring into non-traditional forms such as carpet, clothing, plastic sheets, or glass is a growing field of interest where traditional electronic design tools are lacking.

The use of inkjet or roll-to-roll screen printing techniques for applying conductive ink to non-traditional surfaces is significantly different from conventional printed circuit board fabrication techniques, and therefore, few commercial tools to design, simulate, or test such designs exist.

[783] Modern designs using these techniques are usually piecemealed together through different programs, such as CAD or Illustrator tools, to simply draw traces and component pads before transferring them to a printer where conductive ink is applied to the target surface. There is also minimal integration with electrical or mechanical simulation tools as the dielectric and mechanical properties of paper, glass, and various plastics vary significantly from each other and traditional laminates. As these types of designs continue to grow in popularity, CAD and EDA tools for layout, part placement, simulation, and manufacturability design checks on non-traditional laminates or surfaces will come to market.

Integrating electrical components and wiring into woven fabric to design smart textiles and wearables without traditional laminates or circuit boards is another area that traditional electronic design tools struggle to support. Flexible textile circuits can be created by weaving conductive metal thread and plastic mounting strips in with traditional textiles. Electrical components, such as sensors or microprocessors, are then secured to the mounting strips. [784] Schematic design of these textile-based flexible hybrid systems is not widely supported by any traditional commercial EAD toolset, and design problems such as electrical resistance and fraying of the conductive threads and tearing or separation of the electrical components from the mounting strips during active use make simulation and testing of smart textiles difficult. [785] Co-design tools, such as Co-eTex, currently address the lack of full design tool customizability with a standardized base circuit design in woven textiles that can then be modified with snap-on wires and electrical components. Co-eTex supplements this with software tool support to create modified software for attached microprocessors. Restrictive and standardized design environments like this may eventually be replaced with CAD and EDA tools built to support threaded conductors and layout. As design in this realm is conceptually quite different than printed electronics, the look and design flow of the tools will most likely resemble tools from the textile industry rather than from traditional electronic design.

6.7 Tools for Manufacturing of Flexible Hybrid Circuits

To physically manufacture a circuit board, manufacturing facilities require data exported from EDA layout tools in a format their fabrication machinery can process. Fabrication of each layer in a design requires an image of the layer's conductive metal, a listing of drill holes, and the type and thickness of dielectric laminates used between layers. For conventional rigid electronics, most designers have their tools export this information in the form of Gerber and ASCII drill files, a file format that originated in the 1960s and contains only the minimal information needed to plot metal layers of a printed circuit board. However, as more complicated fabrication techniques such as embedded components, variable layer materials, and multiple stack-up regions have become common place with flexible hybrid circuits, the need for a more comprehensive standard manufacturing file format pushed the development of IPC-2581. [786]

IPC-2581 is a manufacturer independent file format that natively includes manufacturing information about layer stack-up, laminate and cover layer materials, drilling sizes and locations, electrical nets, components listings, and design documentation. [787] Most modern commercial EDA tools already support exporting into the format (or ODB++ a proprietary competitor), and future tools should be expected to continue implementing new additions to the standard in order to support additional flexible material types, strain reliefs, masks, panelization options, etc.

Manufacturers use the IPC-2581 or ODB data as input into their Computer-Aided Manufacturing (CAM) tools that physically operate the manufacturing equipment. The CAM tools provide design for manufacture (DFM) feedback based on the specific machinery capabilities of the facility and enable manufacturers to easily modify designs as required. Current commercially available CAM tools, such as Frontline's GenFlex, are specifically designed for flexible laminate circuit boards and support flexible circuit specific features such as design checks of bend regions, adhesive air-gaps, stiffeners, copper tie-down creation, and embedded components. [788]

6.8 Design Automation and Future Design Tools

As seen with the feedback loop between design and simulation tools, an optimal design of modern electronics to meet requirements in mechanical and electrical performance, manufacturability, and reliability is quickly proving itself intractable for human designers to handle without resorting to iterative designing via test and check. The added complexity of board and component mobility in flexible hybrid circuits only further complicates the design process. In the near future, flexible or rigid components embedded in the flexible substrate will continue to complicate the thermal and mechanical modeling of designs.

Future advancements in automated computer design and simulation tools for both rigid and flexible electronics will be required to continue to move the human designer further up the hierarchical design process and speed up both development and test time. High performance flexible circuits of the future will simply be too large and complicated to design without the power of automated computer design assistance. Further, with active and passive components embedded in the substrate and mounted above and below cover layers, the potential EM interactions between complex and dense electrical interconnects will begin to massively complicate design performance. In the near to medium future, it is unlikely to completely remove the human from the details of designing flexible circuits. However, as computer processing power continues to advance and design tools become more integrated, much of the tedious manual design entry and test will be performed by EDA and CAD tools, leaving the human designer to write high-level specifications and requirements, verify simulation outputs, and focus on manufacturing.

TECHNOLOGY GAP: DESIGN TOOLS FOR FLEXIBLE HYBRID ELECTRONICS

As circuit designs become more complicated, there is a need to start to move away from the designer manually entering each individual flex region and corresponding design constraints.

POTENTIAL SOLUTION

The opportunity exists for programmatically defining layer stack-ups, appropriate copper routing rules in flex regions, and electrical and mechanical simulation feedback in design tools for flexible electronics. Generate higher level requirements documentation which an EDA tool implements with feedback from simulation

TECHNOLOGY GAP: DESIGN TOOLS FOR FLEXIBLE HYBRID ELECTRONICS

There is a gap in simulation tools that offer comprehensive and integrated mechanical, thermal, and electrical simulation of boards across the full range of supported flex and motion. Separate tools exist individually, but they don't account for potential design issues resulting from the combination of simulated scenarios.

POTENTIAL SOLUTION

Develop an open architecture, open source platform for simulation and EDA tools so that these products are developed and materials and concepts change they are easily added or adapted and users can integrate the software products.

TECHNOLOGY GAP: DESIGN TOOLS FOR FLEXIBLE HYBRID ELECTRONICS

An opportunity exists for improvement of simulation tools when using embedded components in flexible substrates. Components embedded between layers of silicon and metal shielding will behave differently with regards to electrical, mechanical, and thermal performance from surface mounted parts, better integration and support from simulation environments is needed.

POTENTIAL SOLUTION

Develop simulation tools that will account for the mechanical, electrical and thermal changes to a device as it is flexed and operates under conditions for which it is being developed. This should include but not be limited to the effects of flexing a device, extreme operating temperatures (hot and cold), vibration, and thermal shock on a device.

TECHNOLOGY GAP: DESIGN TOOLS FOR FLEXIBLE HYBRID ELECTRONICS

There is a gap in design tools for non-traditional flexible electronics such as those mounted on textiles, paper, glass, ceramic, diamond, etc. Most of the designs are done with tools not specifically designed for these materials, or extreme operating conditions, and lack the needed functionality and manufacturing support given by design tools.

POTENTIAL SOLUTION

Develop design tools that can adapt and use non-traditional materials and component parts for flexible electronics. These would include but not be limited to those materials in the above list. Thought should be given to a dynamic platform that could accept materials as they are developed or new uses are found for traditional materials.

7.3.0. FLEXIBLE HYBRID ELECTRONICS CAPABILITIES, DEVICES, AND APPLICATIONS

FHE is a pragmatically-driven, multi-faceted technology platform targeting unique *evolutionary* solutions in compact form factors (size, weight, and power – SWaP) by bringing the best practices of conventional packaged technologies in electronics, photonics, MEMS, and communications to flexible surfaces. From the pragmatic point of view, FHE is a technology platform where rigid printed circuit boards are abandoned in favor of flexible, lighter, and cheaper substrates, especially in low-cost, portability-first applications. In a wider perspective, it is also possible to view FHE as a natural product of the rapid expansion in device miniaturization and nano-materials in the first decade of the 21st century, and an extension of ongoing system-level integration in nanotechnology and additive manufacturing approaches. In this broad perspective, FHE embraces and integrates all creative solutions that can be implemented on these novel surfaces as long as they result in a substantial advantages in terms of functionality, cost, size, weight, connectivity, operability, and serviceability. These traits are highly-desirable for both defense and consumer applications. Thus, FHE can be considered a game-changing technology, especially when printed devices and systems become more capable and comparable in performance to current on-chip integration. Whatever the perspective, it is counterproductive to limit the scope of such a vibrant and fast-developing platform as FHE. Projecting from previous waves of technological advances, efficient solutions can impact all walks of life in a remarkable fashion. Accordingly, this report is open to both the pragmatic and the broad perspectives on FHE as it projects into the next 25 years of development in related applications, especially for defense-related themes.

It must be mentioned that *printed electronics*, one of the frequent components of FHE systems, appears to receive the majority of the attention and limelight in academic R&D circles, owing to its greater research potential and implied novelty. Yet, practical FHE systems that are of interest to the FHE Manufacturing Innovation Institute [789] and industry in the short term are unlikely to utilize purely printed devices in great numbers. Printed devices may be limited to specific solutions in power generation (solar & battery), displays, interconnects, and antennas, thanks to compact, low-profile, and flexible ICs that can now be transferred/assembled directly on the host surfaces. On the other hand, the *hybrid* nature of FHE systems is likely to have a larger impact in the short term to improve performance by employing mature IC technology and pushing its limits. An effort was made to place sufficient focus on the more narrow and pragmatic perspective on FHE because of its more immediate impact on applications. Nevertheless, the study did not forfeit the broader perspective and future opportunities that are enabled by ongoing advances in printed and organic electronics.

Figure 62 shows several examples that illustrate what the technical community currently describes as FHE: example (a) is a generic schematic of an FHE system; [790] examples (b) to (e) are real examples of FHE devices from UKPETEC, American Semiconductor Inc., IMEC, and the Rogers research group at University of Illinois at Urbana-Champaign (UIUC).

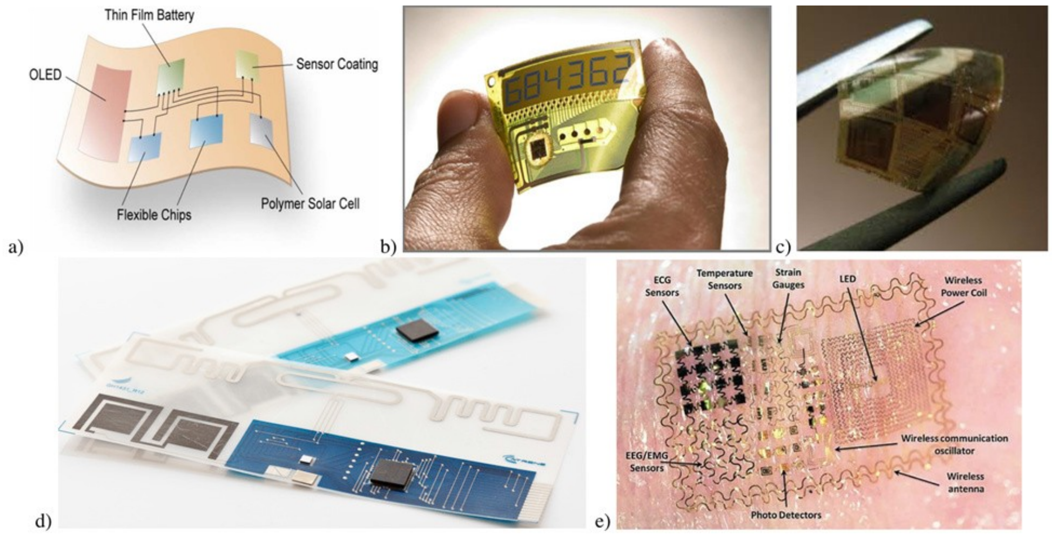


Figure 62. Examples of FHE Devices

7.1 Assumptions for FHE Development

This section is essentially a disclaimer for the inherent limitations of the predictive analysis in this part of the report. Given the volatility of epic proportions in world markets, dramatic developments in socio-political landscapes in recent years, approaching uncertainties in once well-established trends in technology, and incredibly rapid advances in micro/nano devices and systems, predictive technology analysis is as hard as it gets. However, using the proven potential of FHE technologies and the increasing dependence of the world economy on information-driven societies, it is still possible to hypothesize, or at least speculate, in a methodical manner.

To set the stage for estimating the possible pathways for the development of FHE technologies and applications, the study team made the following assumptions.

End of Conventional Moore Trends by 2025:

Although time and time again, Moore's law has prevailed against imminent showstoppers, the fundamental barriers of physics, materials, manufacturing, and economics jointly dictate that conventional scaling have limited 'technology nodes' to deliver, 10 and 7nm being currently in sight. In other words, the practical end to Moore's scaling is likely to occur in the next decade. Hence, by 2025,

- CMOS device scaling will stop at gate lengths between 5 and 10 nm.
- CMOS devices alone will not determine the limits of high-performance computing (HPC), although they may still drive the memory market.
- A new form of post-CMOS device technology will emerge to drive the HPC market so that conventional CMOS architectures will come down in cost for custom design of specialized classes of sensors and transfer print devices.

FHE Development in Three Stages:

To describe the likely development of FHE technology platform in most general terms over the next 25 years, the study team envisions that FHE will develop in three distinct generic phases:

- Short Term (2015-2022): 1st Generation FHE systems and products
- Medium Term (2022-2030): Mature FHE systems and products
- Long Term (2030-2040): Intelligent and Agile FHE systems.

Unique features of these phases and how they evolve are described in some detail in the remainder of Section 7.0 and will constitute the backbone of this predictive analysis.

Custom On-Chip Design Superior to FHE:
It is presumed, at least throughout the short and medium terms of FHE development listed above, that conventionally integrated, custom-designed chips on inorganic, solid- state substrates will outperform FHE products in terms of real estate requirements and achieved speeds. In other words, FHE will not produce higher-performing custom solutions for the most part, even though it may result in substantial savings in many of the figures of merit. This is also to say that the sum of parts in the heterogeneous FHE technologies will not be greater than the whole, outperforming a properly designed and integrated conventional IC, despite the unique advantages that it may bring. In the long term, however, this may change, especially when FHE includes disparate technology elements that cannot be otherwise integrated on the same substrate surface, and its truly hybrid nature confers FHE advantages that cannot be produced by conventional solid- state integration on a given single-crystal substrate.

No Catastrophic Developments in World:
The analysis and projections contained in this report are based on notions of steady-state developments and historical trends. Transient instabilities and extreme developments in the world economy (just like in 2008-2010 and the more recent European debt crisis), the environment (climate, draught), natural resources (depleting minerals and fossil fuels), and socio-political equations (broad regional conflicts and political crisis) may change the course and pace of the described projections. For instance, as late as 2015, most global macro-economic indicators were still on par (if not short of) levels recorded before the housing market collapse and the ensuing banking crisis of 2008-2010. Hence, such lasting and profound crunches in the economy can totally change any analysis or projection.

7.2 Capabilities, Devices, and Applications

Facilitated by the rapid and continuous progress of electronics in the 20th century, today we are presented with unique capabilities: novel materials tailored at the atomic level; efficient computing at our finger tips; sensor systems capable of collecting large amounts of data on the environment, human physiology, and social interaction; and cognitive computing and predictive analytics for effective management of human health and urban infrastructure. Technology downscaling is responsible for low-cost, compact but powerful computational tools already powering today's smart-phones. Tomorrow, these devices will shrink further and seamlessly integrate onto the surfaces of daily items such as paper, textile, and polymers in adaptable, intelligent, ultra-compact, lightweight, and affordable FHE systems customized for a broad spectrum of applications. Because of this, FHE systems have the potential to be the next ubiquitous platform that will provide sensing, communication, computation and connectivity - all integrated into stamp size devices on flexible surfaces that will dramatically change the way humans will collect and interact with information. [791] This exciting opportunity will impact

defense, aerospace, sensing, transportation, biomedical, and consumer electronics, while posing new research challenges.

The 2015 iNEMI Roadmap for the electronics manufacturing industry states that "FHE systems "continue to receive greater attention for near-term commercialization opportunities." In fact, FHE is already growing at an explosive rate, is designated by the National Academies as a target for "increasing basic funding," [792] and is supported by a number of large national [793] and international [**1**] initiatives as well as larger investments from the global electronics industry and a number of government entities. [794] Within the US, states like Ohio, known for a strong base in polymer science and manufacturing, are rapidly expanding their investments in FHE, as evidenced by initiatives such as FlexMatters. [795]

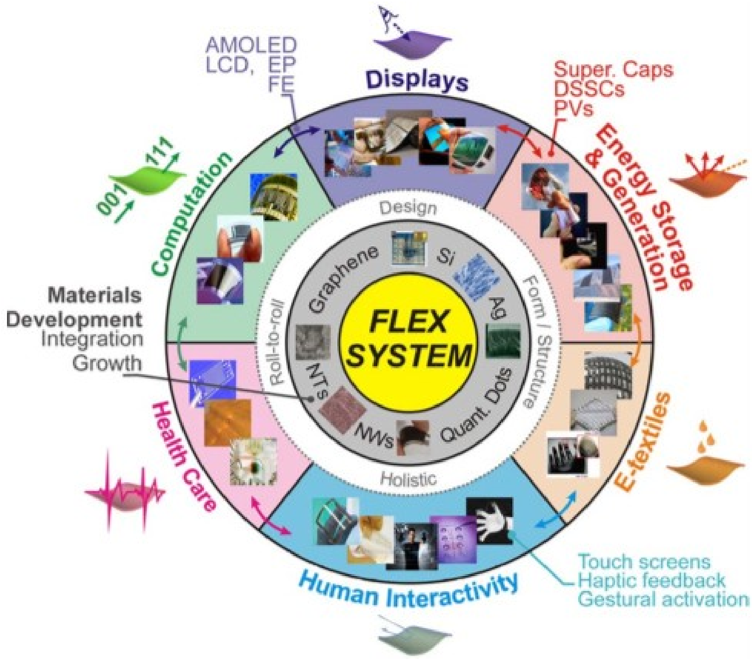


Figure 63. FHE Enablers and Functional Areas [791, 796]

Propelled by advances in printed electronic technology, mobile computing, sensing and gesture/voice recognition, and energy harvesting devices, electronic systems find it ever easier to get out of rigid and static forms that limited their use to unique environment and locations. As illustrated by Figure 63, flexible electronic (FE) systems can be built for variety of applications and explore many novel materials and devices. Yet, the true potential of highly integrated FE systems applied to a broad range of complex problems in defense and civilian domains such as distributed real-time computation, biomedical instrumentation, chemical sensing, education/training, supply-chain management, and transportation remains largely unaddressed. This report attempts to summarize major developments in FHE systems, which are currently emerging at a fast pace, and to identify potential opportunities and strategic alignments in technology development and military applications.

7.3 Existing Capabilities: The Toolset

A general review of the existing 'toolset' that empowers and drives FHE development is provided in this section. The nature of this toolset not only indicates the building blocks of

existing FHE systems, but also underlines necessary elements and components required to construct more capable FHE systems in the future. Identifying these elements enables a good appreciation of the forces that are likely to define future opportunities and applications in FHE development.

From a minimalist perspective, it can be argued that there are three elements that empower all successful FHE systems: (1) A *substrate* that allows flexibility, facilitates integration and permits reliable operation; (2) a *hybridization or heterogenization* layer that encapsulates the 'ready' functional elements that can be incorporated to boost performance; and (3) the more nebulously defined *interconnectivity* layer that enables delivery of signals and power between the previous two. These are briefly introduced and discussed in the next three sections, followed by sections that describe and present examples of various devices, processes, and technologies that make FHE possible in several application areas. It must be emphasized that the summary below does not focus on the fabrication, printing, assembly, and packaging tools applicable to FHE. Many of these tools are available mature technologies and are studied in the earlier sections of this report in sufficient detail.

7.3.1. Substrate for Integration

A flexible substrate is the basis of an FHE system, and is used for assembling and integrating all necessary components in a given application. The substrate can be made of plastic, paper, wood, skin, textile, or other materials, and its selection will often have strong implications with respect to overall signal quality, heat management, and level of flexibility and weight of the FHE system. Polymer materials are attractive for use as substrates due to the ability to tailor their electrical and mechanical properties, and the existing base for scalable manufacturing. Table 30 compares the essential properties of common polymeric substrate options.

While a detailed comparison of polymeric substrates is beyond the scope of this report, it suffices to point out that surface hydrophilic/phobic behavior, roughness, and chemical stability are key parameters, besides heat conductivity and physical elasticity, for the choice of polymeric substrates for FHE systems. Many FHE system components such as displays, batteries, and RF sensors are most readily printed and tested on polymer substrates such as PET, polyamide (PA), and polyimide (PI) layers that provide a good compromise among most requirements. As a result, these materials are expected to prevail in the short to medium terms, until more resilient, flexible, cheaper, and easier to process alternatives become available.

Table 30. Comparison of Common Polymer Substrates [798]

Property	PET	PAcr	PEN	PC	PS	PI
Tg (°C)	70	105	120	145	203	270
Upper Tm (°C)	115	175	268	115-160	180-220	250-320
CTE (ppm/°C)	33	70	20	75	54	8-20
% Transparency	90	>90	88	92	89	35-60
Water Absorption (%)	0.6	0.2	0.4	0.25	1.4	2-3
Y. Modulus ($10^9 N/m^2$ Gpa)	2-2.7	2.4-3.4	0.1-0.5	2.6	-	2.5
Solvent Resistance	Good	Good	Good	Poor	Poor	Good
Surface Roughness	Poor	Fair	Poor	Good	Good	Good
Dimensional Stability	Good	Good	Good	Fair	Fair	Fair

Table 31 presents a similar, though qualitative, comparative summary for textile materials, which are currently undergoing a rapid expansion for FHE applications. Textile substrates present unique capabilities and may be especially useful for integration into clothing and infrastructure of interest to both defense and civilian applications. Paper/plastic substrates are not feasible for some of these applications, for example in some cases where a human user is the carrier of the FHE system. Electronic textile (e-textile) surfaces are relatively behind in terms of FHE integration as compared to polymer/paper substrates, but are expanding at an extraordinarily fast rate. Therefore the gap is expected to close rapidly, given the breadth and depth of the worldwide textile industry. As summarized in Table 31, e-textiles currently present serious options for assembly of FHE systems, utilizing a broad range of tools that are becoming as mature as the printing techniques summarized in Figure 64. Thus, textile-based PCB integration should not be excluded as a potential avenue in the future expansion FHE systems.

Table 31. Fabric Circuit Board Fabrication Techniques [799]

Type	Characteristic Elements	Advantages	Disadvantages	Flexibility	Connection
Couched circuits	Conventional wires insulated by a layer of non-conducting thread	User conventional wires	Lacks flexibility	Low	Mechanical attachment to conventional connector
Woven circuits	Alternating conductive thread and insulating fibers	Can be automated, or made in a hand loom	Connection of electrodes to PCB	High	Mechanical attachment to conventional connector
Knitted circuits	Conductive fibers on non-conductive knit	Machine / automated	Additional yarn requirements	High	Varies on conductive thread chosen
Embroidered circuits	Conductive yarn sewn into fabric	Flexibility	Needs to be crafted	Medium	Snap grippers
Conductive ink circuits	Patterned conductive ink	Can be masked	Endurance	Medium	Conductive glue/liquid conductive ink
Fabric PCB (iron on)	Layers of conductive and non-conductive fabric	Flexibility; can be soldered to wires	Elaborate handcrafting	High	Soldering terminals
Thic film process	Silk screening of conductive ink, glues, and conductive polymers	Straightforward path manufacturing	Tendency to brittleness	Medium	Sub-Miniature version A (SMA) soldered connectors
Thin film process	Sputtering of Au particles	High resolution of paths	Specific fabrication environment	Medium	SMA soldered connectors

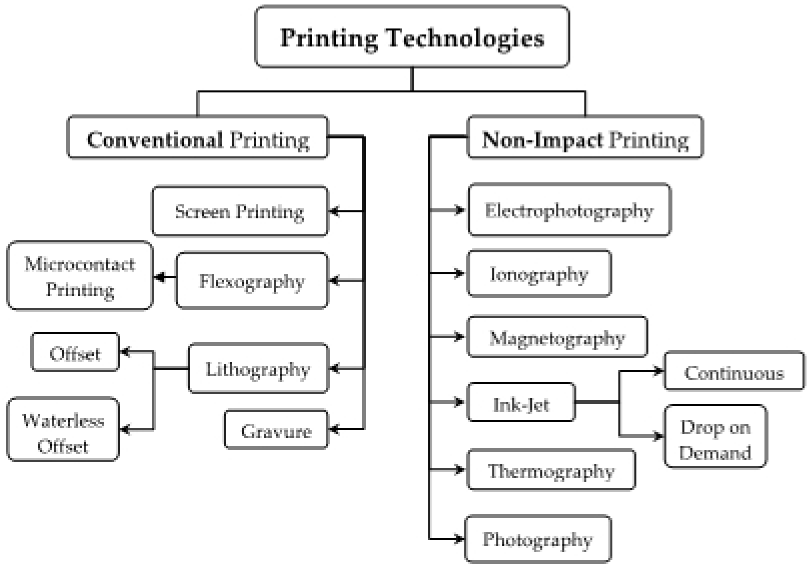


Figure 64. Classification of Common Printing Technologies

7.3.2. Paper Substrates

A similar comparative analysis for paper substrates is not easy to produce, given the vast variety of paper pulps and their possible combinations. Paper substrates tend to be cheaper, less resilient, rougher, and prone to humidity absorption, which reduces their applicability to printing solution-based processes and demanding DOD applications. However, in laminated substrates, paper can easily be integrated with the polymer substrates in a cost-effective manner. For instance, based on the experience and know-how in the paper-based packaging industry, it is possible to build a laminated paper substrate with a polymer surface optimized for printing on one side and a metal foil surface ideal for RF applications and cooling on the other. Hence, hybrid paper / polymer / metal composites or laminated paper/foil substrates are likely to offer remarkable solutions on the substrate requirements, since they can have optimum weight and cost, and offer more environmentally friendly options. Moreover, it is possible to utilize paper surfaces' sensitivity to humidity and ability to wick solutions and analytes for biomedical applications, an aspect lacking in polymeric or inorganic (metal or amorphous films). [800] Hence, especially for biomedical applications and sensors, paper may present unique substrate options, where all other electronic elements are transfer-printed or built on laminated surfaces. In other words, despite its limited physical and chemical resilience, laminated paper substrates may gain importance in FHE applications that have 'wet' biomedical sensor needs and composite FHE solutions that require multiple substrates together. In this context, it would be fair to point out that the same opportunity may exist for laminated textile surfaces, although the cost may be higher.

7.3.3. Hybridization & Heterogenization Layer

Individually packaged sensor devices, ICs, and sub-systems that implement specific functionalities make up this layer. These could be made up from existing off-the-shelf surface-mount devices, or from custom ICs that are transfer printed and enveloped in specialized flexible packages. These components often determine the hybrid nature of the system and its performance limits, since it is possible to bring on an entire conventionally-integrated system using novel hybridization schemes such as wafer thinning, transfer printing [801], or substrate spalling [802], as shown in Figure 65.

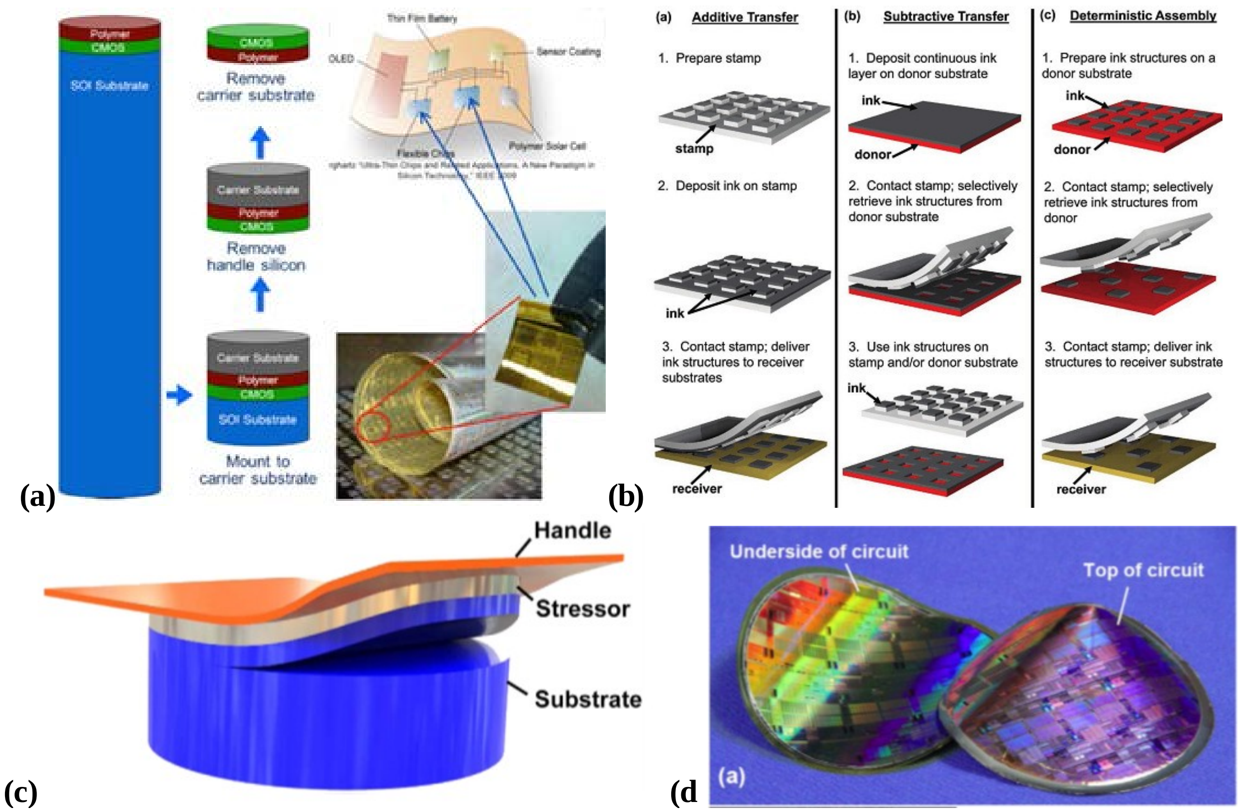


Figure 65. Hybridization Examples: (a) Transfer Printing; (b) Mount and Etch [803]; (c) Spalling [802]

Figure 65 also summarizes common transfer approaches and other material sets that can utilize transfer techniques. It is important to note that many of these approaches are also used in advanced nanofilms, graphene, and membrane transfers for building many standalone flexible devices, not just for full ICs. Therefore, it would be wrong to simply consider this layer as the conduit to bring conventional electronics onto flexible surfaces. Instead, it is a platform to incorporate any technology that cannot, for one reason or another, be printed directly but should be included in the FHE design to enhance performance. When viewed from this broader perspective, it is clear that the hybridization layer can become a liberating element. As such, it is obvious that novel flexible *packaging technologies* can greatly impact this hybridization and heterogenization layer. Similarly successful 3D IC integration can also impact the development and complexity of FHE systems through this layer. Therefore the heterogenization layer, with its ability to incorporate conventional devices and complex sensors through chip overlays or packaging technologies, is the true performance booster in many FHE systems. Bringing the best of two worlds, conventional or proven versus fledgling and novel, this layer determines most performance characteristics and differentiates printed electronics from true FHE solutions. It also relates to the narrow/pragmatic definitions of FHE as well as to its broader perspective. Many novel materials, sensing elements, and applications of FHE can be enabled by this layer after they have been sufficiently proven and matured.

7.3.4. Interconnectivity Layer

This layer comprises the input/output (I/O) and interconnect infrastructures that enable sensing, routing, and transfer of information and power, often in the form of printed conductors, displays,

antennas, and inductive, capacitive, resistive, and sensing/coupling physical devices. In many cases, the density and capability of this layer determines the overall system complexity and agility and the power levels that the system can handle, and they also define how the system will interact with its environment. Of the three basic elements of an FHE system, the interconnectivity layer is the most open to innovation and novelty, given the many device types, sensors, and elements that it can incorporate. This is especially true for many of the future innovations in flexible devices that are individually printed on substrates to test given new material, sensor, display, battery, and/or antenna technologies. The impact of the new technology on the FHE system can be repeatedly tested through this layer until the technology reaches maturity and reliability levels that can rival those of pre-packaged devices or alternatives. Figure 66 and Figure 67 provide examples of interconnectivity layers in a few FHE systems. Application examples can be greatly expanded for interconnectivity layers, given their vast range of possible elements. The examples chosen here are simply intended to introduce the context of the interconnectivity layer and explore how this layer can rapidly expand the complex domain of FHE applications. These are by no means the limits of this layer; it will be explored more thoroughly in the following sections.

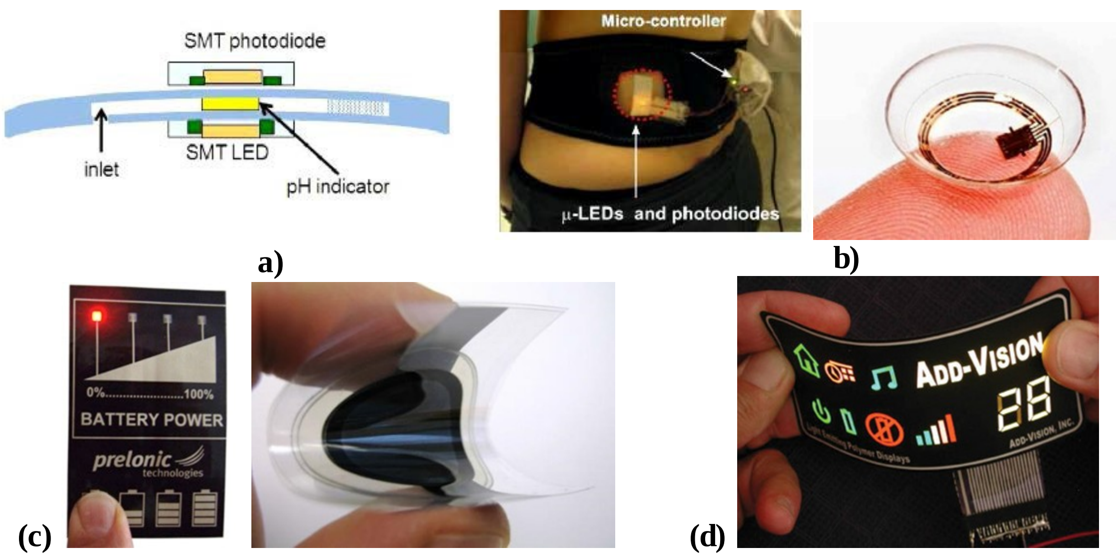
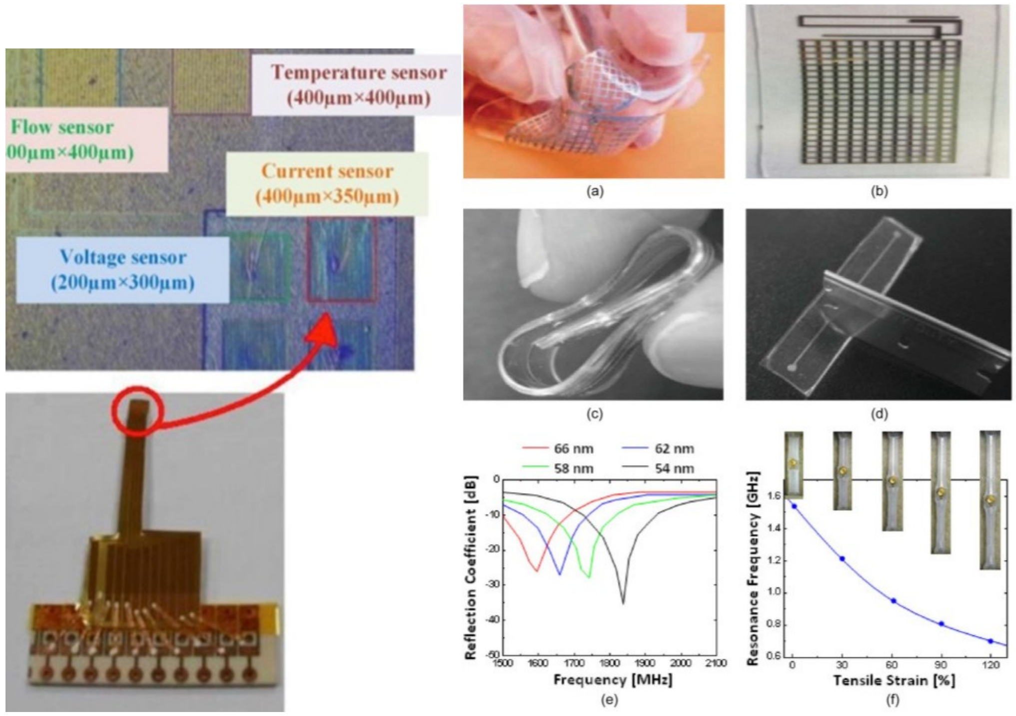


Figure 66. FHE Interconnectivity and Integratio Layer Examples [804, 805, 806, 807]



(a) **(b)**

Figure 67. Essential Interconnectivity and Integration Layer Elements: (a) Sensor Banks [804]; (b) Foldable Printed Antennas [791]

7.3.5. Integrated Circuits and System Adaptation

FHE systems typically draw attention due to their unusual form factors and flexible substrates that allow them to be integrated into applications that are inaccessible to conventional electronics. However, it has become clear that organic (printed) electronics that are intrinsically linked to the flexible technology are not adequate in terms of performance and power for many critical consumer and defense applications. Although very rich and successful in alternatives for sensing, display, battery, antenna, and power applications, printed devices are not able to compete with even standard Si CMOS technology, let alone faster, more capable semiconductor alloys in terms of electronic switching and storage technologies.

Neither the present organic conductors or semiconductors nor more exotic, layered or composite materials containing graphene, CNT, or nanoparticles of various types can yet rival the complexity, scalability, noise rejection, or robustness found in standard chip technologies. While this may change in the medium to long term, it is unlikely that these new alternatives will beat conventional nano-scale chips in the short term. As a response to this major drawback, and as an example of the creativity of the R&D community that is behind flexible technologies, two major approaches have been developed to adapt or transfer entire chips onto flexible substrates: *Wafer thinning* [809] and *transfer printing* [810], [801]. In both approaches, first, an entire CMOS system is built on standard Si bulk or SOI substrates, using all advantages of the latest silicon BiCMOS technology. Then, for this full-scale chip to be included as an add-on flexible structure, the substrate is either thinned to approximately the one-micron level using standard etching, polishing, and cleaving techniques, or mounted onto transfer wafers that ‘exfoliate’ or ‘lift’ them by the aid of polymer-based handling layers as well as sacrificial etching layers. Either way, the

end product is a fully capable and functioning CMOS chip (typically an entire controller, memory, and so on) existing on thin (≤ 1um) silicon layers that can be bent and strained and are, to a great extent, transparent.

In the case of much smaller (~ 1x1mm) and cheaper chips (such as amplifiers and power modules), it is also possible to mount as-is ICs directly onto flexible substrates using the *flip-chip bonding* approach. That can provide a cost-effective solution [810, 812] and greatly expand the types of circuitry that can exist on an FHE application.

Besides flexibility, IC adaptation can grant other features to the FHE applications that cannot be easily replicated in conventional circuits. This includes the opportunity to incorporate seemingly incompatible technologies on the same surface at a minimal cost and the ability to transfer ICs on pre-stretched surfaces that can provide additional flexibility for expanding and deformation. [814] Moreover, target surfaces can even be perforated surfaces that allow better cooling and/or 3D-printed complex surfaces that enable tight fitting on enclosures that would be inaccessible for printing or assembly. To illustrate the capability of the various techniques that are available for adapting CMOS onto a flexible surface, several basic approaches are now presented.

7.3.5.1. Wafer Thinning

Wafer thinning is a valuable technology that can facilitate the adoption of full ICs into a given FHE system by reducing the substrate thickness to the 1 to 10 micron level. A prime example is the controlled spalling technique developed by IBM, which is illustrated in Figure 68. [802] In fact, this method can also be applied to conventional solar cells as well as to aerospace applications, since it can cut down weight and radiation sensitivity even in standard applications. Yet another, less pronounced advantage of wafer thinning is its broad applicability; as long as the substrate can be controllably cut-away, etched, and polished, the technique can be applied to substrates other than silicon.

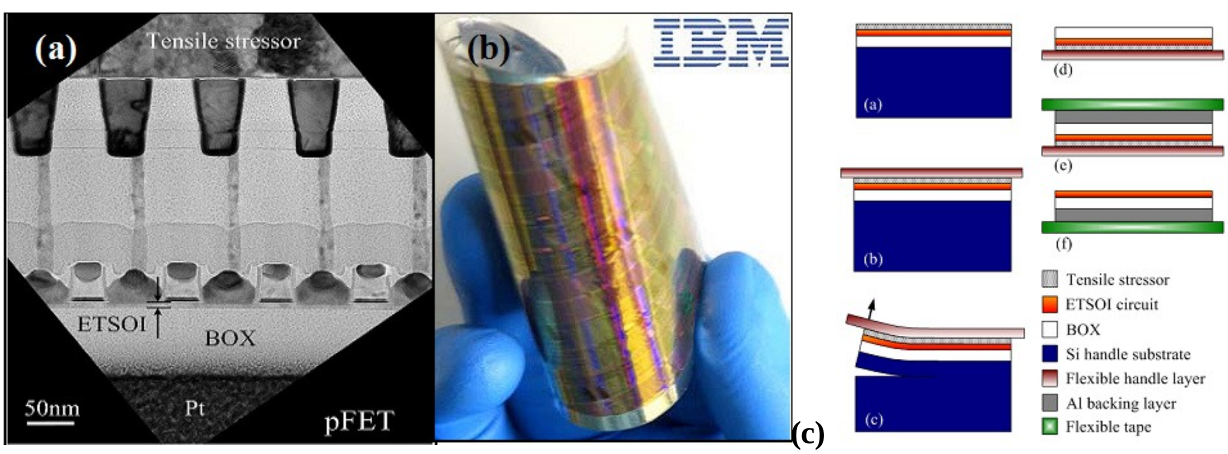


Figure 68. Controlled Spalling Approach by IBM [813]

7.3.5.2. Transfer Printing

In transfer printing, the top active layer of silicon (typically 100 to 1000nm) that contains the CMOS circuitry is cleaved, lifted via handle layers or wafers that first attach or bond themselves to the active device surface, and then used as a vehicle to transfer on to the target surface. This is facilitated by sacrificial layers or pre-strained interfacial layers that lead to eventual separation of

the targeted layers. Since the original wafer has a fresh surface and much of its original thickness, this method has the added advantage of lowering substrate cost. Given that, in principle, the process can be applied to expensive III-V semiconductors or even pre-made nanofilms or 2D crystals such as graphene and/or MoS2, it can be conjectured that transfer printing can greatly expand the FHE application space and lead to substantial cost savings. Figure 69 shows several prominent device results that take advantage of this wafer thinning technique.

7.3.5.3. Composite Approaches

In practical FHE applications that contain complex mixed-signal heterogenization with multiple chips and sensors, it will most likely be necessary to take advantage of the benefits of all possible chip adaptation approaches. It would be unrealistic to expect all suppliers to use either identical substrates (bulk Si, SOI, III-V, etc.) or similar processes. The approaches below are taken from various examples that exploit both wafer-thinning and transfer-printing methods to build slightly more complex 'composite' cases that can be important for future FHE development.

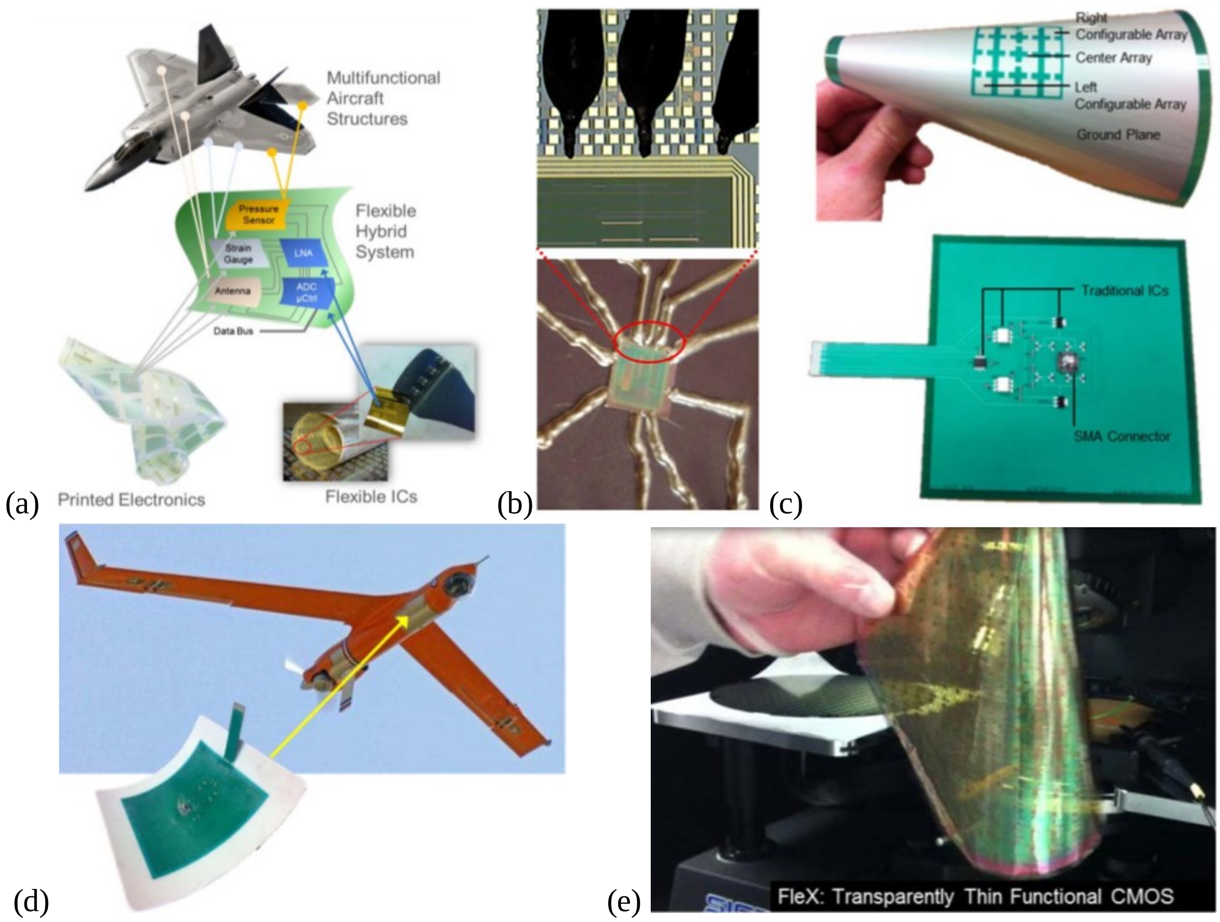


Figure 69. Wafer Thinning & Transfer Printing Examples [803, 790, 815]

In the US, probably the best examples of composite IC integration have been developed by a University of Illinois at Urbana-Champaign (UIUC) group led by Professor John Rogers. That group utilizes a very creative range of FHE systems developed by integrating multiple ICs and printed devices on various substrates and forms. Some examples of the UIUC group's pioneering

work can be found in Figure 70, Figure 71, and Figure 72, which include conventional as well as more exotic implantable, on-skin, and on-daily-tools applications. The UIUC group's work has not only led to novel techniques to fabricate and integrate FHE systems, but also helped illustrate and expand their application domains. A unique aspect of the UIUC group's activity is their extensive use of various stamping techniques, combining them with direct printing and wafer thinning approaches where needed. Moreover, the group also pioneers many bio-medical and DoD-related research projects where they integrate FHE systems with wearable sensing and monitoring applications.

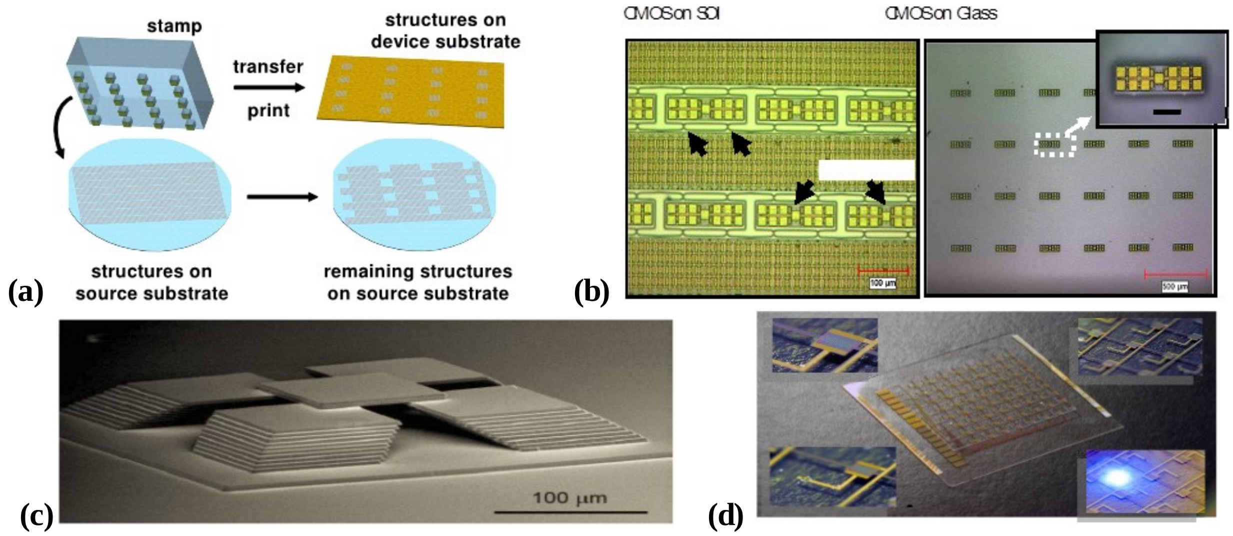


Figure 70. IC Adaptation/Transfer on Flexible Substrates [816]

Stretchable and Epidermal Electronics - A unique FHE application that the UIUC group leads is the stretchable and on-skin printed CMOS systems (see Figure 71 and Figure 72) that utilize pre-patterned (perforated) and pre-stretched polymeric handle layers for CMOS transfer. The resulting stretchable substrate is not only very light, low-weight, and agile, but it also allows unprecedented amounts of bending, stretching, and deformation. It also enables miniaturization for inclusion into very small enclosures as well as biomedically relevant surfaces/spaces, where solutions and air need to flow. This can be readily exploited both in consumer and defense applications, where human skin can be used to assemble the final FHE system with wireless communication as well as optical displays, all which has been successfully accomplished by the UIUC group and has already been funded by DoE, DOD, and other federal agencies.

Low-Profile and Layered FHE Systems - Another unique aspect of the UIUC stamping-driven approach for FHE assembly is its applicability to many different devices and chip technologies, while also allowing multiple layers of integration on top of each other, as illustrated in Figure 70. This leads to very compact systems and can help reduce cost, especially in consumer applications that also have a broad appeal for this technology.

Since transferred ICs drive performance limits and establish the upper power ratings, they can be considered 'critical' to the success of FHE solutions. This is true especially in the short-term, given that the available substrates, assembly/printing techniques, and types of inks are still being explored to a large extent. Accordingly, there is a wide international interest and multiple centers

of activity abroad that should also be kept under scrutiny to fully track development of this critical technological approach. For instance, a European effort thins the wafers partially, and then utilizes etching as well as a handle wafer to transfer-print CMOS-compatible devices, as shown in Figure 73. Employing this technique Dahiya and co-workers transferred a number of large area sensors and small ICs and verified device integrity and system operation on bent surfaces. [809]

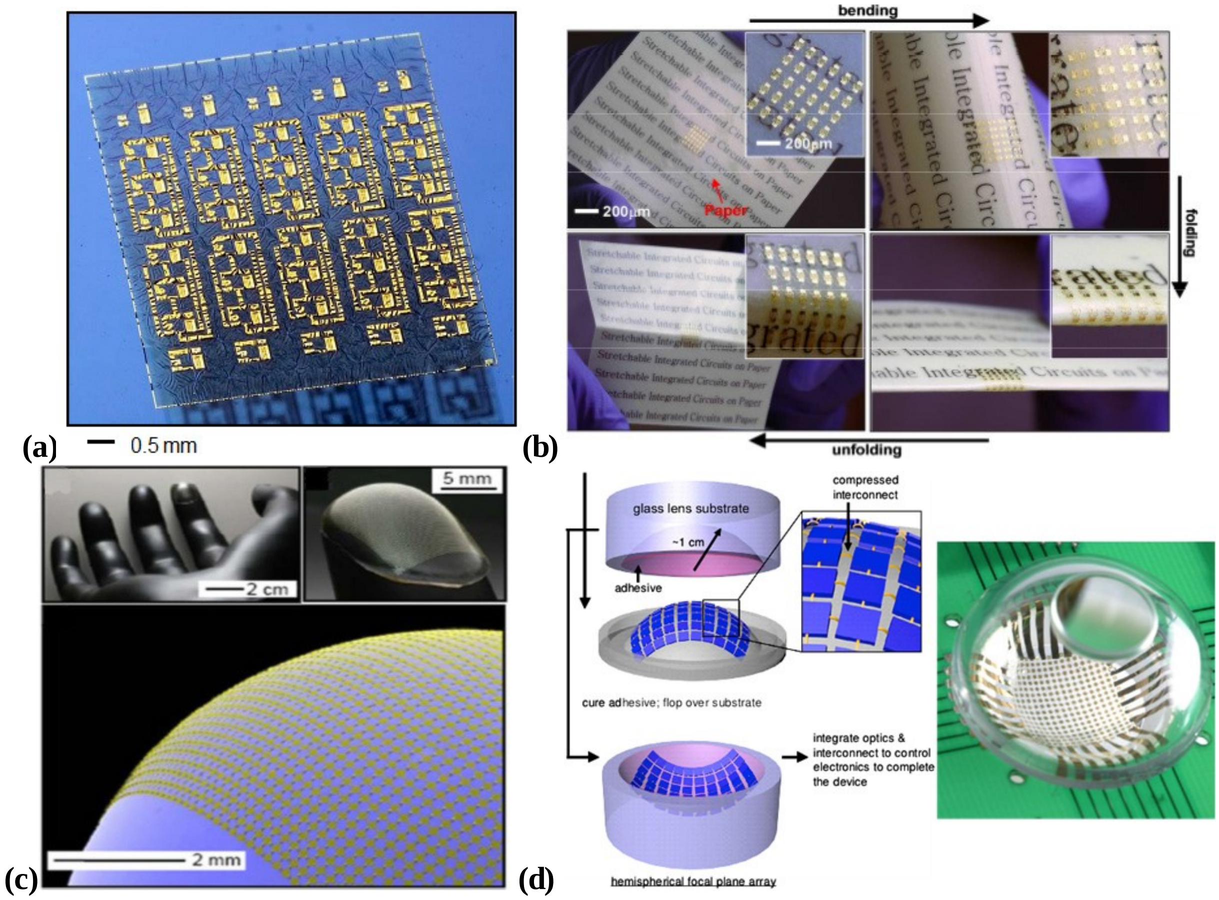
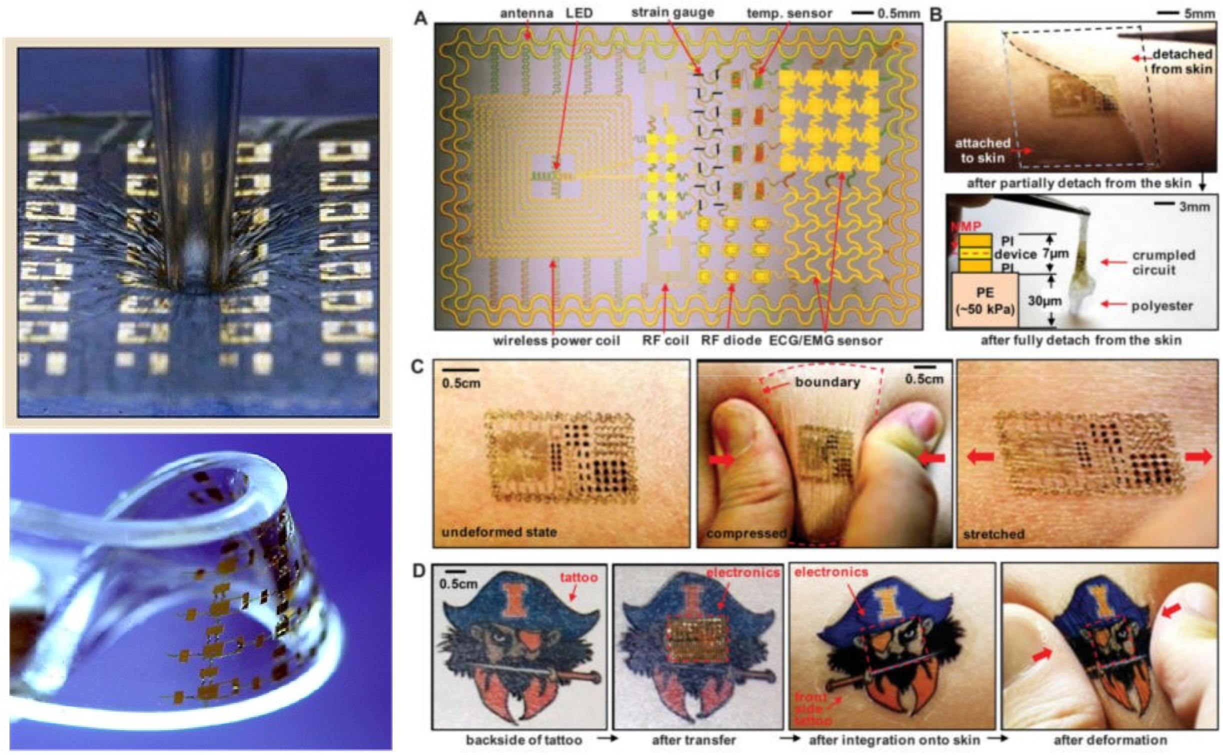


Figure 71. Stamp Mediated Transfer-Printed (a-b) and CMOS on Paper and (c-d) Non-CMOS Devices on Polymer [816, 817]

Beyond CMOS for FHE - There is a final and important factor to emphasize about IC integration and adaptation techniques. Although these techniques are currently optimized for present day IC technologies (Si CMOS and mostly optical III-V processes), they are not fundamentally limited by any of them. As the nanomaterials and devices revolution runs its full course, novel devices on even more exotic surfaces can also be incorporated into the FHE designs via similar adaptation techniques. For instance, graphene-based devices that are assembled on Copper surfaces can be easily and surely incorporated into FHE applications. This provides substantial cost savings (re-use of substrates), access to ultra-fast but low-power RF and other devices important for defense applications, and many other important devices (e.g. sensors, antennas, and displays) that can be built. Using rapidly expanding and maturing graphene technology or other 2D crystals such as BN, MoS2, WS2, and NbSe can bring a wealth of device options and sensor capabilities. [818] Therefore, it is important to visualize transfer printing or

IC-adaptation technologies as a general vehicle to carry any new advance in a seemingly different technology platform onto FHE systems. As a result, future FHE systems can take advantage of any non-CMOS device or system component as long as they can be 'lifted' across using these transfer/adaptation vehicles.



(a) (b)

Figure 72. Composite Integration for (a) Stretchable and (b) Epidermal Electronics [816]

TECHNOLOGY GAP: CHIP ADAPTATION & TRANSFER

A general, low-cost, and scalable chip transferring/adaptation process that can be used also on compound semiconductors is needed to accelerate FHE product developments.

POTENTIAL SOLUTION

Independence on the type of wafer used in the transfer printing or thinning process is necessary along with development of new tools and standards such as reduction on substrate thickness and introduction of sacrificial layers in compound substrates akin to buried oxide in SOI.

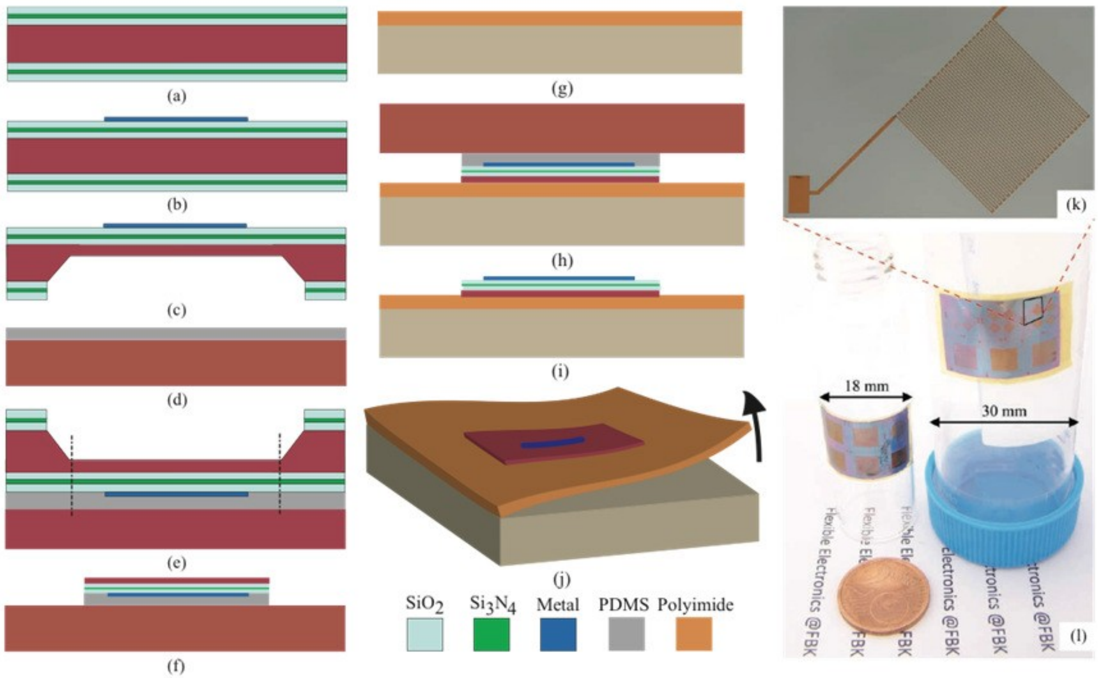


Figure 73. Transfer of CMOS-based Sensor Designs onto Flexible PI Substrates [809]

7.3.6. Thin-Film Transistors, Fully-Printed CMOS Systems, and Memory

Flexible transistors are crucial components for nearly all applications of FHE systems. In general, transistors can be used to perform several functions and have many applications, including creating logic gates and logic circuits. [819] Switching speeds and mobility are very important for transistor performance, and the higher these values are, the more operations that can be performed in a certain timeframe. Miniaturization helps to increase the switching speeds, but as the channel lengths decrease with miniaturization, short-circuiting tends to increase. Therefore, tradeoffs have to be considered. Inkjet technology and most lithographic techniques do not typically allow for extremely small channel lengths, but they still enable excellent performance at channel lengths of 0.1 – 10 µm. If the channel lengths need to be smaller (<100 nm), some specific types of inkjet printing and nanolithography can be used.

Just like almost all other electronic devices, conventional transistors are based on inorganic material technology. However, as demands for thinner and flexible electronic devices have become more prevalent, transistor technology has started to investigate other materials and processes. One innovative approach is to develop techniques to make traditional inorganic transistors thinner, thereby innately increasing their flexibility, as discussed previously in this section. Another approach is to use materials that are more flexible to begin with, such as organic materials like carbon-based compounds and polymers. Thin-film transistors created from these organic materials will not reach high-performing commercial applications. Instead, they simply need to be "good enough" for other application. [819] They will likely see use in low-cost, high-volume areas, such as RFID tags and displays, because these areas will not require expensive circuitry and will allow for printing methods to be used. Organic transistor active matrices have already been demonstrated for large-area stretchable sensors and LED displays. [820] Some of the best performing organic transistors have been observed with small molecule organic materials, such as pentacene and rubrene. [819] Additionally, AFRL has been focusing on bio-

based materials to create bio-FET devices. [821] High organic transistor performance has been achieved with a graphene transistor using metal oxide dielectrics. [819] These transistors have been demonstrated to achieve higher mobilities and lower channel lengths than state-of-the-art transistor technology.

Although still inadequate in terms of performance for high-end applications, printed thin-film transistors (TFTs) have shown rapid and significant advances, especially in the last decade. [818, 824, 826] Improvements include mobility reaching 15 cm2/Vs, reduction of parasitics (contacts and gate overlaps), minimization of gate length via edge patterning techniques, as well as creation of complementary *p*- and *n*- type devices that allow building of CMOS digital and analog circuitry by direct printing, as exemplified in Figure 74. For instance, Takeya & Uno recently demonstrated a complete directly printed CMOS system operating at 15.6MHz. [827, 828] This creates the possibility of extremely low-cost, environmentally-friendly CMOS electronics that can be built by direct printing such as low to medium scale integration of full-electronic systems (memory circuits and controllers in particular). Directly printed CMOS circuits should not be viewed as a competitor to the previously introduced transfer-printed ICs, but rather cheaper and easier alternatives for applications that cannot afford, for one reason or another, integration of a real IC on a chip. Of course, in the long term, if or when mobility of organic semiconductors can rival amorphous silicon or even crystalline thin films, the experience gained from directly printed CMOS on flexible substrates will become extremely valuable. Until then, very high-end applications of interest to the aerospace and defense industries will be on transfer-printed CMOS.

A unique advantage of directly printed CMOS devices and circuits is the ability to mix and match active channel materials such as conductive polymers, semiconducting metal oxides (ZnO, CuO, In2O3 etc.), or novel solution based semiconductors nanoparticles, to form a CMOS thin film transistor pair optimized for a given application. [824, 829] In other words, although the performance may not be stellar, dielectric and structural properties of the printed CMOS can be reasonably easier to optimize than those of standard Si CMOS transistors. This can be an advantage, especially for sensor and memory applications. It may even be possible to optimize *p*- & *n*- type transistors to separate sensors by employing two different channel materials or gate stacks. Therefore directly printed CMOS circuits can still offer unique features that can make them an interesting and cheaper choice when performance is not the defining attribute.

As directly printed CMOS develops, it also will invariably improve the performance of all other printed devices such as passive RLC elements and diodes, while reducing parasitics and thus the overall power budget currently dictated by transfer-printed ICs. For future FHE development, if direct CMOS printing can deliver even mediocre performance at ~100MHz level, this can have profound consequences for useful functions including wireless communication as well as cost and power limits. Therefore, especially in the medium-term of FHE development, direct CMOS printing should be carefully studied and may become a game changer.

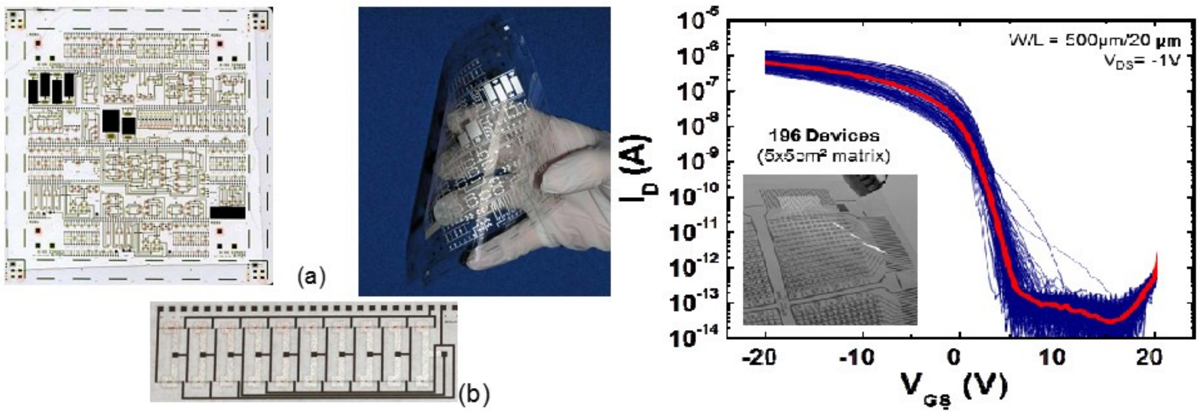


Figure 74. Low-Scale Integration of CMOS Systems by Direct Printing of Organic TFTs [828]

<u>TECHNOLOGY GAP: FULLY-PRINTED CMOS</u>

No sufficiently dense or fast fully-printable CMOS technology exists today at the 1GHz performance level. If achieved, this would lead to direct printing of CMOS circuitry using low-cost approaches and can make FHE systems even more capable, reduce manufacturing costs, and allow a wide range of embedded controllers to be implemented on flexible substrates.

<u>POTENTIAL SOLUTION</u>

Novel high-conductivity organic semiconductors, or ultra-thin film ambipolar transistors with nano-material (CNT, graphene, Ag, or Si nanowires, etc.) channels that can be produced reliably as p- or n-type complementary devices may pave the way to >1GHz organic circuits.

As many computing and computing-related devices become flexible, the need for flexible non-volatile memory (memory that is stored when power is cycled) has increased. From a device perspective, the necessity for all components to be flexible, lightweight, low power, etc. is critical. Further, flexible memory is a critical component of future flexible devices because memory is fundamental to operation – as code storage, data storage, and as dynamic memory when needed. A significant amount of research at the university level, and in industry, has occurred involving flexible memories.

Non-volatile memories can be classified into capacitor-type memories, transistor-based memories, and resistor-based memories. [830] Resistive random access memory (RRAM), ferroelectric random access memory (FeRAM), flexible flash memory, and ferroelectric field-effect transistor (FeFET) memory are considered the strongest candidates for next-generation, flexible memory devices. Graphene has attracted considerable attention as a candidate material due to its unique properties.

Nantero, Inc., located in Woburn, Massachusetts, has developed an alternative memory chip based on CNT technology. [831] Their product, called NRAM®, is created by forming a film of CNTs on a standard silicon substrate. The substrate contains an underlying cell select device and

array lines (typically transistors or diodes) that interface the NRAM switch. The NRAM acts as a resistive non-volatile random access memory (RAM) and can be placed in two or more resistive modes depending on the resistive state of the CNT fabric.

NRAM is as fast as and denser than dynamic random access memory (DRAM), is nonvolatile like flash, has essentially zero power consumption in standby mode, 160 times lower write energy per bit than flash, and is highly resistant to environmental forces, including heat, cold, magnetism, radiation, and vibration. [831] Nantero envisions that their technology will be used to replace flash memory or DRAM, and in the future they expect to be able to store terabits of data on a single memory chip.

One benefit of NRAM is that it is compatible with existing CMOS fabs without the need for new tools or processes. [831] It requires a small number of process steps and only one mask layer, allowing it to be fabricated at lost cost. NRAM is scalable down to 5 nm, and is compatible with both 3D multilayer architectures and multi-level cell (MLC) operation, making it applicable for the next generation of memory technology. Ideally, the chips based on Nantero's technology can be used in a wide range of markets, including mobile computing, wearables, consumer electronics, space and military applications, enterprise systems, automobiles, the IoT, and industrial markets. [832]

7.3.7. Antennas

In order to provide wireless connectivity, integration of flexible antennas to FHE systems operating in specific frequency communication bands is a must. In fact, wireless data transfer and monitoring is the key reason to opt for FHE systems in most applications. However, each application places strict limitations on antenna size and performance. These antennas can be built on paper and plastic using conventional lithography or inkjet printing, or using conductive textile cutouts and embroidery on textiles. In general, antennas for FHE systems have weight and size advantages, while their changing geometry, low dielectric constant, thin substrates, vulnerability to humidity, and lower-than-bulk conductivity place limits on their performance. It is important to realize that advances in building antennas of various complexities and characterizing their performance and reliability almost invariably generate knowledge to also improve other important passive devices, notably inductors, which are important for RF operations and wireless power transfer and can be crucial in certain FHE applications and RFID tools.

Because of their relatively large and simple structure, compact antennas of various types (patch, broadband, plasmonic, phase-array, and so on) are one of the prime devices that can be found in most FHE systems. Since the alternative conventional antennas are rather limited in terms of SWaP, printed antennas not only serve as the key elements for wireless communication, but also offer tangible advantages for FHE systems that are not possible from other technologies. Moreover, Analog/RF CMOS systems that can be built in sub-32nm technologies require antennas that are typically very large to be efficiently built on the chip level. This issue can be effectively resolved for FHE systems by using directly printed structures (the interconnectivity layer mentioned in Section 7.3.3) on antennas. Together with displays and batteries, printed antennas provide a strong case for why FHE can deliver solutions that are not otherwise possible.

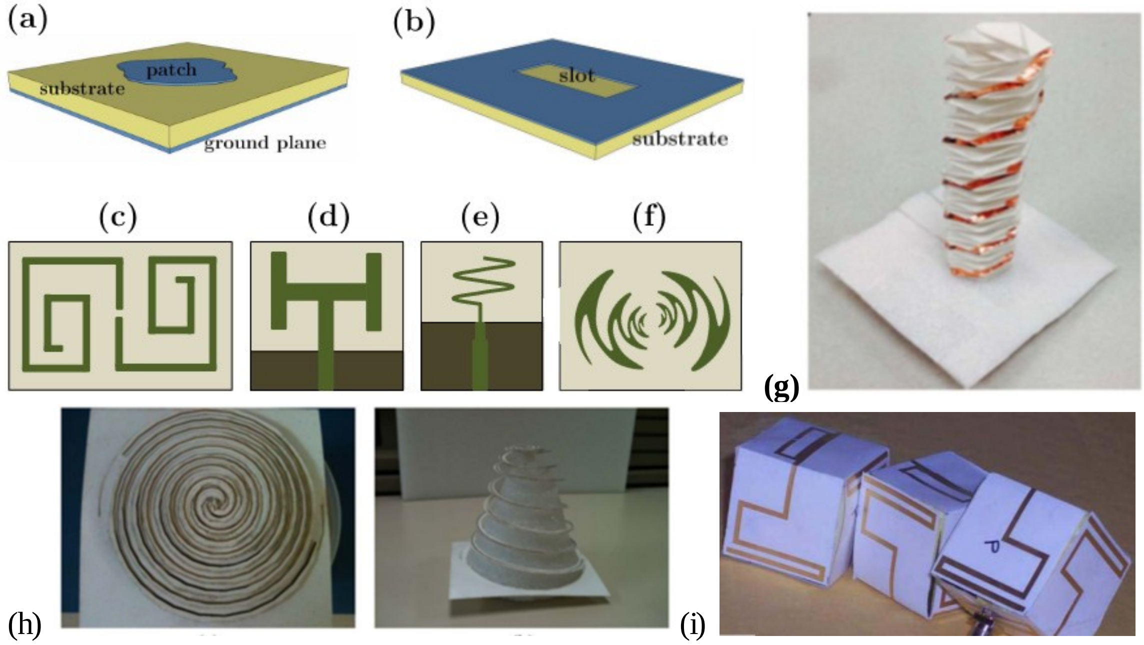


Figure 75 Planar (a-f) [833] & Non-Conformal, Folded, & Complex (g-i) Form Factor Printed Antennas [840]

Almost all basic antenna types have been considered for printed electronics on paper, plastic, or textile surfaces. There is a very broad range of device examples on such flexible surfaces, with frequencies from several tens of MHz to tens of GHz. It can be safely said that antenna technology is one of the earliest and largest beneficiaries of printing technologies, even though reliability, accuracy, and flexible operation characteristics are always suspect. Several good reviews (see references [833-839]) have been used to produce the following summary, which focuses on unique features of several examples.

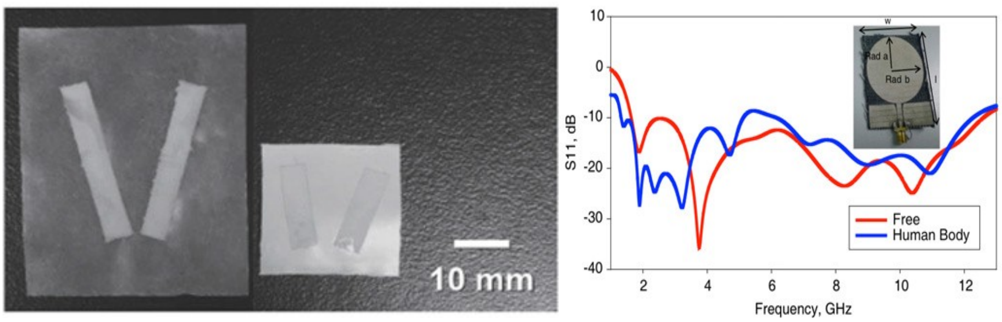
7.3.7.1. Various Printed Antennas

Depending upon the applications and characteristics, there are many types of printed antennas, as indicated in Figure 75(a)-(f). These include micro-strip, slot, and coupled-inductors (in case of RFIDs). The availability of high resolution printing processes allows most such printed structures on paper and plastic possible. However, many industrial planar or R2R printing systems are actually limited in resolution around roughly 10 microns at best, which means that typically these antennas operate at the < 1GHz frequency range unless conventional patterning (lithography and etching) is used to produce the < 1micron resolution needed for 2-5GHz operation.

7.3.7.2. 2D/3D Folded Antennas

Because of their fixed shape and characteristics, traditional antennas lack the ability to adapt to changing system requirements. The ability to reconfigure the antenna as desired would likely reduce the number of antennas required for a particular application. Usually, diodes and phase shifters are used to change the bandwidth, radiation pattern, and frequency of operation of an antenna. Another approach, origami folding, can be used for shape changing antennas that are ink-jet printed on flexible substrates. [840]

An axial mode helical antenna is shown in Figure 75(g) that can change its operating frequency band by changing its height. Keragami is another derivative of origami, which involves cutting and gluing in addition to folding. Using this technique, a spiral antenna is made into a conical configuration or strip antenna on a cubical platform that contains an FHE system, as shown in in Figure 75(h)-(i). As the spiral antenna is made into a conical shape, the gain of the antenna is increased. The main challenges with these antennas are the need for manual reconfiguration and mechanical support. To overcome this, smart flexible materials like Shape Memory Alloy (SMA) can be used. The SMA remembers its original shape when deformed and returns to its original shape when heated. Therefore the height of the antenna can be increased by passing DC current through it. When the current is removed, upon cooling, the structure comes back to its original height. [840]



(a) (b)

Figure 76. Flexible antenna: (a) dielectric scaling using high-k media (paper) [841]; (b) performance on textile before and after placed on body [842]

7.3.7.3. Flexible Dielectric Scaling

The easiest approach to obtain a miniaturized antenna is by shortening the length of the antenna. The antenna length must be one fourth of the wavelength of the radio waves being emitted/received, to achieve resonance. The radiowave's frequency depends on the dielectric environment: it decreases upon transfer from air into a *high-k* material. [841] To achieve the desired outcome, a *high-k* nanopaper can be used as the dielectric, as shown in Figure 76(a). In this case, the *high-k* silver nanowire paper composite shortened the wavelength from 115mm to 68mm. The length of the antenna was reduced by half while maintaining the original flexibility and sensitivity. [841] Hence, specialized flexible and porous substrates can be used to bring a new feature to antenna manufacturing that is not easily achieved on conventional silicon or metallic substrates.

7.3.7.4. Antennas on Textiles

Even though, technically speaking, antennas on e-textiles are not printed antennas, they can benefit from FHE advances are already being deployed on uniforms, protective clothes, recreational gear, and so on, to provide wireless communication capability. Textile-based antennas are also used extensively in the medical field for monitoring ECG and the working of lungs, monitoring patient vital parts, etc. Figure 76(b) shows results from a 2014 study that explored the response of a circular patch ultra wide-band antenna. As compared to their free-standing counterparts, on-textile antennas worn by a human user typically have a wider insertion bandwidth which also shifts to slightly lower frequencies. As the user moves and re-orients parts of their body, a tightly tuned narrow-band antenna would suffer performance losses, not to

mention the change in the orientation of its primary propagation direction. Hence, given the dynamic orientation and deformation that an on-body antenna can experience, broadband designs with low-gain are more desirable for on-textile antennas.

On-textile antennas can be built by sewing in pre-cut conductive textile elements, patterned from conductive threads using digitized embroidery machines, or even directly printed using various printing approaches adapted on polymers. Despite their unique advantages in terms of ease of manufacturing, larger size, and simplicity in positioning, wearable antennas still present challenges. These include the fact that most woven textiles with large gaps in their structure have low dielectric constant, variations in thickness, significant surface wave losses, and increases in bandwidth. [834] In addition, the thickness and density change at low pressures because of the flexibility of the textile. To reduce these effects, suitable textiles can be integrated with a flexible polymeric substrate to achieve the desirable electromagnetic characteristics.

TECHNOLOGY GAP: BROADBAND AND STEERABLE ANTENNAS

Given their flexible nature and multiple-domains of use, broadband and steerable antennas on FHE systems would allow them to become more adaptive to user needs and less sensitive to changes in environmental conditions.

POTENTIAL SOLUTION

Beyond simpler static antennas, reconfigurable antenna structures, multi-feed or phase-array based antennas on flexible substrates would greatly enhance adaptive capabilities of FHE systems.

7.3.8. Displays

Perhaps the most 'spectacular' elements of FHE systems, and a feature for which they are mostly recognized in the popular press, are the vivid, lightweight, foldable, emissive polymer-based displays that can rival the best conventional counterparts. All in all, flexible organic displays, along with antennas, are probably the most mature flexible device technologies. They have an existing market of their own and a broad industrial base for large-scale manufacturing and integration. The iNEMI roadmap on large area flexible electronics lists the following application categories of flexible displays: electronic signs and billboards; point of purchase/sales; portable consumer electronics, including mobile phones; e-books; touch panel controls (human machine interface); GPS and electronic maps; automotive displays and instrumentation; avionics displays; wearable displays; and smart cards. [843]

To a large extent, it would be reasonable to assume that flexible displays require the least critical investment for the development of mature FHE systems, thanks to the existing industrial products and know-how. The first flexible display devices were produced by Xerox PARC in 1974 and were eventually marketed as electronics paper display technologies in the early 2000s. Additional researchers in electronic, paper-type flexible displays include Hewlett-Packard (in collaboration with Arizona State University), Plastic Logic (Germany), Sony (Japan), LG Electronics (South Korea) and AU Optronics (Taiwan). Research work in flexible displays has largely shifted to organic light emitting diode (OLED) technology. There is still plenty of room for development, especially with respect to cost, power levels, and reliability. For harsher

environments of interest to military users, there are many mature examples that can show reasonable performance for FHE systems, as illustrated in Figure 77. What makes the case for displays even stronger for current and future FHE applications is the ability to form both small and large area displays at very high resolution that are not easy to replicate in other technologies.

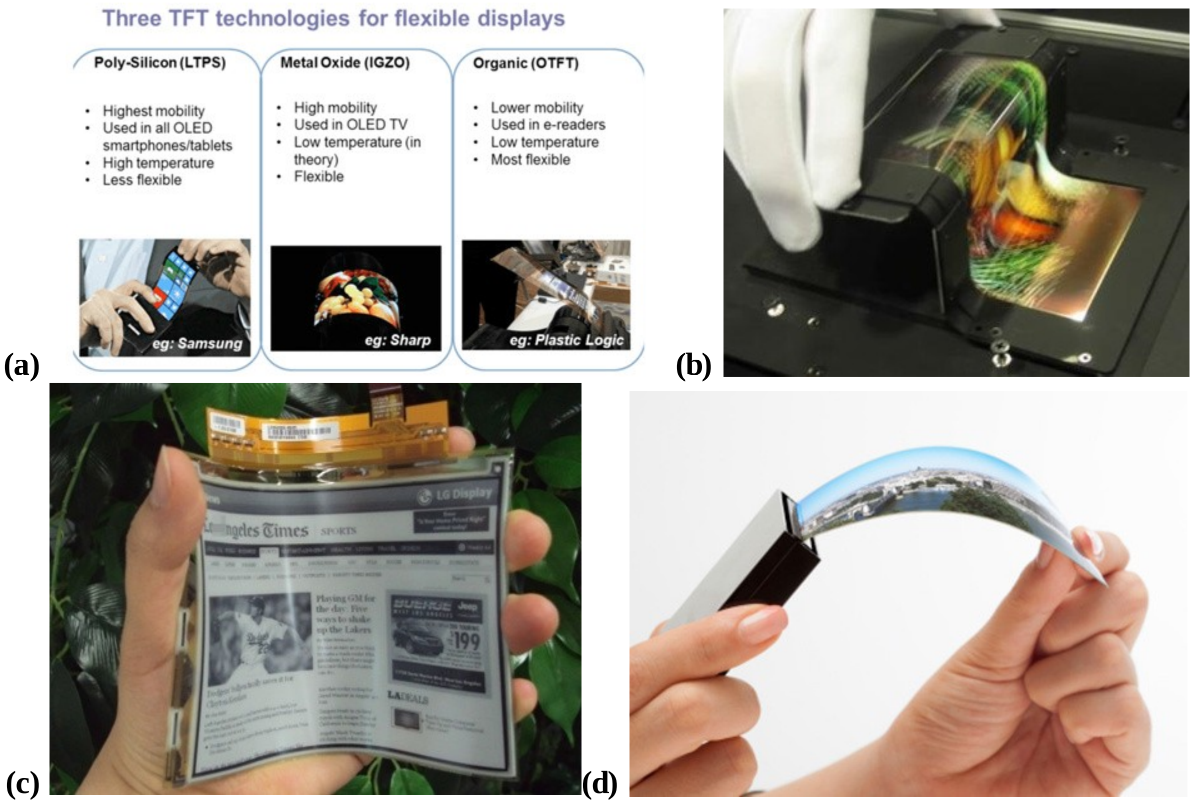


Figure 77. FHE Displays by Nokia Labs (b) [835], LG (c) [836], & Samsung (d) [837]

In Figure 77, several noticeable examples of display technologies that are relevant to FHE applications are provided. In fact, the same display technologies are already in use on glass substrates for consumer applications, and are in transition to flexible substrates, which is the reason why the display technology is mature in the first place. Ultra-thin films of polycrystalline silicon deposited with novel low-temperature techniques, metal-oxide based inks, or organic conducting polymers may be used for the addressing elements. OLED has distinct color and contrast advantages, even though its speed and reliability should be improved before it can match more mature counterparts that have higher mobility.

***LED Illumination and FHE* -** From the FHE perspective, display devices are mostly ready solutions, much like battery technologies, that have strong market drivers on their own. For most FHE applications, the display size would be small, and power consumption would be the utmost concern, making *e-paper* type reflective displays still the natural choice for most daylight applications. For higher performance, emissive high-contrast displays, the high-paced developments driven by the smart-phone market virtually assures that affordable high quality displays are always within reach. An exception to this case might be in ultra-low-power emissive displays that can be built using OLEDs or exotic metal-oxides driving specialized LED colors in combinations with phosphors.

Since the LED market is expected to make larger market penetration, lighting applications, compact organic illumination devices, and glowing surfaces can be considered as interesting opportunities for FHE, especially in consumer applications. For instance, ultra-light and low-cost water disinfection modules that utilize UV-LEDs might be especially important applications in the unsanitary conditions found in field work and natural catastrophes, as well as in developing parts of the world where the infrastructure is inadequate. Low power and flexible surfaces with transfer-printed UV-LEDs can also be crucial for any bio-medical analysis where dyes are used for identification of molecular/protein groups or tissues. Therefore, high-efficiency UV/blue LEDs may become a target device for flexible-hybrid integration, which cannot be efficiently emitted from organic substrates/polymers in most cases anyway, and transfer printing may be the most effective approach.

TECHNOLOGY GAP: ORGANIC LEDs for LIGHTING & ILLUMINATION

Diffusive illumination or glowing surfaces powered with organic LEDs could have a dramatic impact on illumination and lighting solutions. Current organic LED technologies are optimized for display applications and high contrast imaging. However, a real opportunity also exists in general dimmable and color adjustable glowing surfaces in both defense and consumer applications.

POTENTIAL SOLUTION

Potential solutions for this market can come from ultra-low loss contacts using nano-materials and/or graphene-based nanoinks, higher efficiency organic LED with prolonged lifetime and resilience, and ultra-low cost and large-area LED manufacturing.

Coupled Solar & LED modules - Further discussed in the power section, in many FHE applications the available area might be limited, especially in wearable systems, such that using a large solar cell and display may not be possible. Even if that were possible, there are all the practical and engineering reasons why a vertically coupled stack of LED/Solar cell stack makes sense, such as lowering cost, saving power, reducing electrodes, and reducing reflective glare that upset contrast in emissive displays. Such structures, known as *photovoltaic organic light-emitting diodes*, have already been documented in the literature [842, 844] (see Figure 78), and are still considered to be in a relatively early development phase.

With the upcoming graphene-based low-resistance transparent technologies as well as higher performance *perovskite* organic PV devices, it will be simpler to improve performance and reduce thickness without increasing contact resistance, thereby providing additional means to pursue these ultra-efficient photonic units in the next few years. It is obvious that FHE technologies could be a large beneficiary of these coupled modules, especially when a customary touch interface on top of such a stack is also included to boost interactivity. As the solar cell and display unit are often the largest functional structures in a given FHE design, a stacked solution is an especially interesting and powerful opportunity to reduce FHE system footprint, which may also reduce their cost substantially.

TECHNOLOGY GAP: INTEGRATED ORGANIC LEDs & PV CELLS

Vertical stacking of organic LEDs with solar cells are proven to be viable devices that can considerably reduce area, cost, and power requirements of FHE systems while also improving display performance and system battery lifetime.

POTENTIAL SOLUTION

Solution examples existing in the literature must be improved in terms of performance and cost. Upcoming high-efficiency perovskite solar cells integrated with efficient OLEDs with lower contact resistance may increase performance while reducing cost.

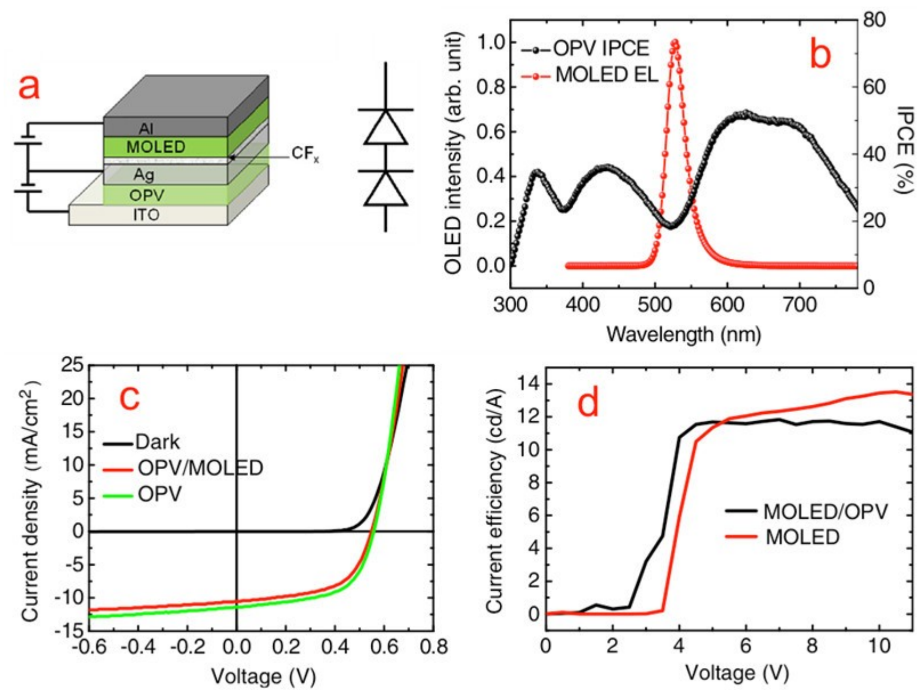


Figure 78. Solar and OLED Combination Device [844]

LED/LCD Displays - EMD Performance Materials is the market leader in liquid crystal materials, a technology that is used for displays, smart windows, smart antennas, and others. [845] EMD believes that the trend for free-form displays will be large LED and LCD displays replacing projector images. These "trending" displays would ideally incorporate several desired features, such as the ability to integrate with the environment, have customized shapes, and allow for outdoor readability, among others. Various industries, including automotive, consumer, and marketing, are starting to demand more enhanced free-form displays. For example, flexible, conformable displays are a desirable technology where space is at a premium and extremely valued, such as in automobile interiors or airplane cockpits.

As with many other areas of the flexible electronics industry, both LCD and OLED have issues to overcome regarding substrates. [845] Thin glass substrates still have limited flexibility, but plastic substrates struggle with high temperatures and permeability. EMD has attempted to address some of these issues by developing high mobility organic semiconductors that allow for

low temperature processing on plastic substrates. Announced in February 2015, Merck and FlexEnable collaborated to develop flexible LCD technology. [846] This new technology will make bendable, light, thin, and unbreakable LCDs possible.

AMOLED Displays - ITRI is developing ultra-thin foldable active matrix organic light emitting diode (AMOLED) technology for mobile device applications. [847] Since 2007, ITRI has evolved their flexible active matrix display technology from active matrix liquid crystal display (AMLCD) to active matrix electrophoretic display (AMEPD) to AMOLED display. Figure 79 shows a comparison between these three different technologies.

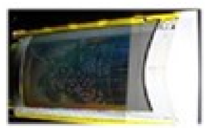
Item	AMLCD (Liquid Crystal Display)	AMEPD (Electrophoretic Display)	AMOLED (Organic Light Emitting Display)
Demonstration	 ITRI, 2007	 ITRI, 2009	 ITRI, 2009
Display Quality	✓ Excellent for video rate	✓ Good for B/W e-paper	✓ Excellent for video rate
Flexibility	✓ Flat & Conformal	✓ Flat & Conformal ✓ Bendable & **Foldable**	✓ Flat & Conformal ✓ Bendable & **Foldable**

Figure 79. Comparison of ITRI's Flexible Active Matrix Display Technology [847]

One of the keys to ITRI's AMOLED technology is their flexible universal plane substrate, FlexUP™, which is a polyimide (PI)-based material that is applied with a slot die coater on a substrate holder. [847] The substrate holder's surface has a de-bonding layer that allows the PI substrate to be removed once the AMOLED structure is created.

Foldable AMOLED technology faces several challenges including increasing the strength and flexibility of the touch panel, creating a thinner polarizer, increasing the performance and flexibility of the TFT on plastic, and handling of the thin substrate material. [847] ITRI is working to address many of these problems in addition to others. They are looking to decrease the polarizer thickness, increase the elongation while decreasing the outgassing of the flexible adhesive used in the system, and improve edge sealing so that delamination issues and barrier properties improve.

It is easy to imagine this sort of lighting system integrated into the fabric of a tent or other portable structure. Combining flexible lighting systems with flexible PV and batteries could create a portable structure capable of generating, storing, and supplying power to an integrated lighting system. The entire structure could be collapsed and rolled up for quick transport and have considerable weight reduction compared to traditional power and lighting systems.

7.3.9. Sensors

Many FHE applications are motivated by the notion that the proposed systems will have easy access to a unique and accurate set of signals (information) by being placed strategically in

environments or locations not reachable by conventional electronics. These signals must be acquired via unique flexible sensors with minimal SWaP footprint, while also being precise, reliable, low-cost, and highly sensitive. In other words, success in many FHE applications is implicitly related to the presence of a broad range of high-performance flexible sensors (temperature, humidity, pH, motion, rotation, acceleration, magnetic, ambient light, etc.) that must be built at specialized material interfaces and surfaces. Thanks to direct and transfer printing techniques, FHE technology has the necessary breadth and depth to offer many of such sensors already either in packaged IC or printed device formats, fulfilling this implicit requirement on sensor performance. One of the most celebrated advantages of FHE systems is their capability to sense, capture, and transduce many chemical and physical signals using compact and novel sensing elements that can be built using diverse approaches. [798, 799, 833, 845-851] In sealed packaging of conventional electronic components, inclusion of multiple sensors in a single CMOS process becomes a difficult task and is often accomplished via dedicated off-chip MEMS sensors, placed away from the electronic measurement or control system, necessitating a specialized data link. Lightweight, compact, and high-performance FHE systems with built-in sensors often do not require this link, and that simplifies design and reduces cost.

(a) (b)

Figure 80. (a) Complete FHE Bio-Medical Sensing Systems [852]; (b) EU's SIMS Project [853]

The Reliability Concern - In exploring sensor examples for FHE applications, there is a fairly large body of work on flexible sensors that can be reviewed, which is attempted in this section. However, many of these examples utilize inkjet printing or patterned thin films that have limitations for harsh environments that are of interest to the defense industry. As a result, a limited set of these 'lighter duty' examples are included in this section. Examples that may be relevant to defense applications are also discussed. Much like in the case of IC adaptation, in applications where robust printed sensors are not possible, existing MEMS products or other packaged sensors may be used to enable FHE systems, albeit with negative effects on power and weight requirements. Undoubtedly, reliability is likely to be a driving issue in the development of new sensors in the medium to long term. A possible solution to this problem lies in the development of substrates that can withstand high temperatures or the use of more inert polymers such as THV, which is a Teflon derivative consisting of a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride.

TECHNOLOGY GAP: SENSORS AND FHE DEVICES FOR HARSH ENVIRONMENTS

Although large number of sensor types and transduction modalities are available to FHE systems, their reliability in harsh environments (extreme temperature, high-humidity, pressure extremes, chemical volatility, mechanical fatigue, and so on) remains a concern.

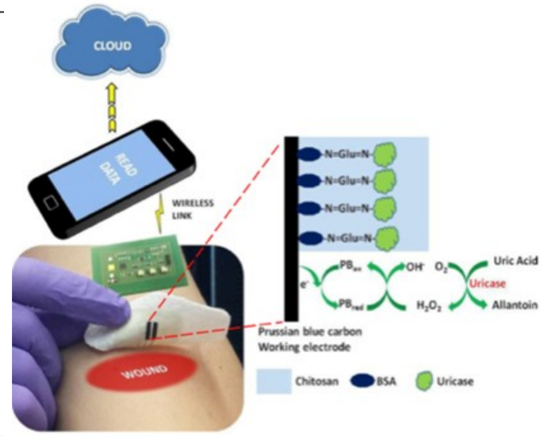
POTENTIAL SOLUTION

More durable polymeric substrates that can withstand high temperatures (≥ 350˚C) and humidity, naturally hydrophobic active surfaces, larger band-gap functional nanoparticle guests in polymeric hosts, and novel sensor architectures that correct for environmental errors may be necessary to improve reliability.

The Integration Problem and the Super Sensing Layer **–** Although there is no shortage in sensing phenomena or device options for building flexible and printed technologies, most of these sensing elements require specialized polymers, thin films, or fabrication sequences that cannot be handled in a single deposition system. In other words, the multiplicity and variety in flexible sensor solutions can become a limitation when the need for compact integration or low-cost fabrication is the driving force for a given FHE application. Thus, to facilitate sensor integration into future, affordable FHE products, the number of 'active' or 'sensing' layers should be limited. A 'super sensing' layer should exhibit sensitivity to as many physical stressors (e.g., temperature, pressure, electrical charge) and chemical species/conditions (e.g., pH, humidity, glucose, cancer markers) as possible to be an effective medium for a broad range of sensor solutions. To this end, many different material alternatives are under consideration: (1) nanoinks consisting of suspensions of metal oxide nanocrystals such as ZnO, AlN, CuO, TiO2; (2) polymer composites that contain ferroelectric or ferromagnetic constituents; (3) PEG-coated nanoparticles of metallic and semiconducting quantum dots; and (4) decorated or paired 2D crystals such as graphene or MoS2; just to cite a few possibilities. Ultimately, this 'super sensing' layer may be an inert and robust polymeric 'host' which can be printed using standard equipment but facilitate solutions that contain functional 'guest' materials or layers that determine the various required sensing responses. It is unlikely that a single host solvent can serve such a broad range of applications, and therefore several such 'super sensing' layers may be necessary.

Given the vast domain of flexible sensors, which is summarized in a number of high-quality reviews, focus in this section is on examples that are most relevant for both civilian and defense FHE applications. Due to its market share and heavy dependence on sensors, the bio-medical field tends to draw more interest in these FHE applications. In fact, as can be seen in Figure 81, the biomedical sensing community has already developed a robust taxonomy for sensors that can be found in FHE systems. These sensors operate within commercial point-of-care devices and rapid response tools that are necessary for field hospitals or search and rescue teams working in stressful conditions.

Type of vital signals	Type of sensor	Signal source
Electromyogram (EMG)	Skin electrodes	Electrical activity of a muscle
Electroencephalogram (EEG)	Scalp-placed electrodes	Electrical activity of brain, Brain potentials
Activity, mobility, fall	Accelerometer	Gesture posture/limb movements
Respiration rate	Piezoelectric/ piezoresistive sensor	Inspiration and expiration per unit time
Heart sounds	Phonograph	Record of heart sounds, with a microphone
Blood glucose	Glucose meter	Assessment of the amount of glucose in blood
Oxygen saturation	Pulse oximeter	Oxy-hemoglobin in blood
Body or skin temperature	Temperature probe or skin patch	Body or skin
Galvanic skin response	Woven metal electrodes	Skin electrical conductivity



(a) **(b)**

Figure 81. (a) Biomedical Sensors, Signals Domain, & (b) Smart Bandage [852]

Example 1 - Smart Bandage: The status of a wound can be determined by the amount of uric acid present in the body. Thus, a smart bandage fitted with an electrochemical sensor that monitors uric acid levels in the wound, which decrease with bacterial population, can help medical care. The changing uric levels are detected by a non-enzymatic sensor with a carbon fiber mesh. [852] In addition, this smart bandage also has wireless connectivity so that the status of the wound can be displayed on a smartphone or a tablet by using affordable RFID or NFC infrastructure. Although this example uses an external electronic board, it is trivial to move such a system onto a single chip and transfer print the final product entirely on the bandage. Carbon electrodes used for sensing are printed via a screen printing technique on a conventional bandage. [852] Carbon electrodes serve as a simple *redox* sensor: urate oxidase oxidizes the working electrode, while hydrogen peroxide is reduced at the electrodes. The reduction current correlates with the uric acid levels in the wound, which is measured by a wearable potentiostat and electrochemical analyzer. In order to prevent contamination by other chemicals or impact on the human body, a biocompatible *chitosan* layer obtained from shell fish is used. The bandage, which operates well under repetitive mechanical stresses, is a robust, sensitive, and efficient solution that can help patients learn the state of the wound while reducing discomfort. As such, it can be readily available for both civilian and military use.

There are other examples of smart bandage technology [855] that aim to detect bad sores before they are formed and damage the surface of the skin. In this case, gold electrodes on plastic substrate are used to form a simple impedance spectroscopy system used by this sensor. [855] Another intelligent bandage that has already been made especially for soldiers is a “paint on” smart bandage that glows to indicate the severity of the wound by the oxygenation concentration. A bandage with a phosphorescent sensor is mounted onto the skin for detection. The phosphor molecules absorb light and glow depending on the amount of oxygen present. Once the bandage is applied to the skin, a protective barrier film is also mounted to prevent oxygen from the atmosphere from interfering and reducing the sensitivity of the device. [856]

Example 2 – Magnetoception: As the name suggests, these sensors respond to an external magnetic field when embedded into an FHE system. Magnetoception is basically a sense that

allows certain animals, such as migratory birds, to detect a magnetic field around them. However, it is not possible for humans, except until these tiny sensors are embedded into the skin via inorganic nano-membranes or polymeric membrane hosts that envelop such flexible magnetic layers. These sensors work on the *Hall Effect* principle, with the Hall Effect sensors made of bismuth on a polyimide (e.g., Kapton) substrate, and can be worn on a finger or used for various e-skin applications. [857] For instance, the finger sensor (see Figure 82) can be used for detection of minute variations in magnetic fields around certain objects or even for *magnetic navigation*. Mechanical deformation reduced the performance of such sensors only slightly, making them ideally suited for flexible applications.

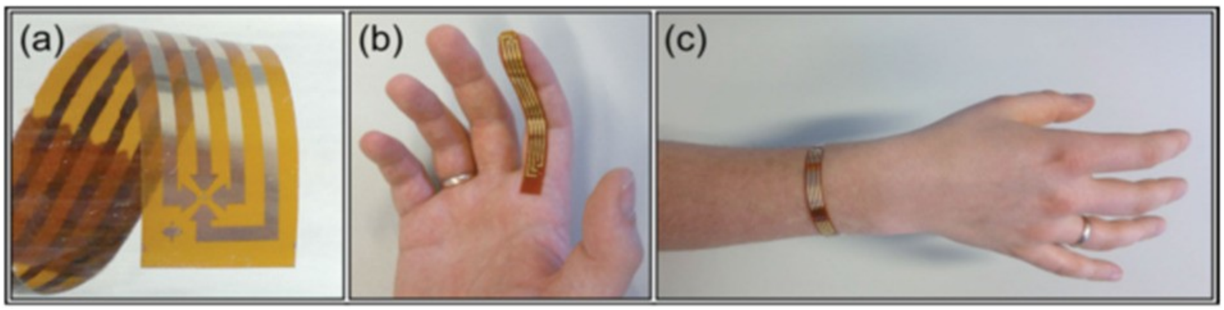


Figure 82. Printed Magnetic Sensors [858]

Magnetic sensors have been the subject of interest around the world, due to their relative stability, broad range of applications, and ease of use. For instance, a Japanese team developed a highly-sensitive and stretchable magnetic sensor less than 2 microns thick that shows no performance degradation from bending or folding. [858] As shown in Figure 83, the ultra-thin and light (~3 grams) sensor can even conform onto the surface of a soap bubble without breaking it and can operate even when totally crumpled. To achieve this level of agility, a pre-stretched elastomer surface is used for deposition, which leads to formation of wrinkles under compression (Figure 83), as was used by a UIUC team's work on stretchable CMOS systems [816, 817].

Figure 83. Stretchable Magnetic Strip Sensor [818]

Example 3 – Smart Fabrics: Flexible electronics on textiles is often associated with wearable electronics. While this is generally true, especially for general consumer products, in principle there is no reason why not to implement any flexible sensors on given fabrics thanks to advanced textile and lamination technologies. Thus, it is possible to empower most fabric surfaces with sensors and utilize them in FHE applications, whether wearable or not, to monitor chemical, mechanical, electrical, or biomedical activities continuously, and to turn sensed information into

actions. Taking an additive approach: the pre-made flexible sensors are to be attached to the fabric or enveloped between layers in this case, which can be limited by available power and physical proximity. It is also possible, however, to knit or embroider a sensor into the textile, which would make it less invasive, permeable for fluids, lighter, and more compact. For instance, Google's Project Jacquard [822] aims to do so and weaves high quality fabrics with conducting yarns that can be finished to form touch-sensitive textiles or other sensors, as illustrated in Figure 84. In other weaving approaches, it is possible to create textile-based pressure sensors using capacitive, piezoresistive, or optical approaches. For example, to make a capacitive type of pressure sensor, the conductive fabric to be used may be coated with a polymer such as a PDMS layer that has very good elastic properties. [859] When placed perpendicularly, these electrodes (conductive coaxial fibers with insulation) form capacitors that can increase when the PDMS dielectric deforms upon touching, as shown in Figure 85. This approach can be readily expanded into a resistive approach with piezoresistive fibers or a single optical fiber routed around a structure or body for the optical approach.

Another interesting application for smart textiles is to warn drivers (or pilots in the case of aerospace applications) who may fall asleep while driving. A heart signal recovered and processed by the FHE system via the textile sensors embedded into the seat can be used to warn the driver/pilot. This very same method can also be used to monitor the heart rate of patients who might be having a cardiac arrest but are not fully aware. Therefore, smart textiles will be invariably popular for biomedical applications that require low-profile, continuous monitoring. [860] Similarly, athletes or physiotherapists can utilize tightly fitted textiles containing fiber-optic threads as extremely accurate and fast motion sensors. These sensors can capture precise biometric data on performance and progress over time, as exemplified by XelfleX [861] products.

Smart garments for consumers are currently being offered by a number of companies, including Ralph Lauren, Heddoko, HexoSkin, CityZen Science, OMsignal, Athos, Gymi, and many more. [863] In general, these garments provide biometric data such as heart rate, breathing rate, walking or running pace, hydration level, and similar metrics. Most of the smart garments offer smartphone or other device compatibility through Bluetooth or similar data transfer methods. Little information is available on the technologies enabling these items, with Ralph Lauren offering only that "biosensing silver fibers are woven directly into the core of the shirt." [864] Some manufacturers indicate sensors woven into the shirt.

Smart garments are also targeting safety applications. R-shirt (France) is marketing a shirt that includes GPS locating for children or the elderly. Smart garments for infants are being pursued by a number of manufacturers, including Exmovere, Owlet Baby Care, My Sensible Baby, and Mon Devices. These smart clothes monitor infant position, heart rate, breathing rate, and sleeping while alerting parents in the event of an emergency. [863]

Ultimately, a collection of these remarkable sensors and smart fabrics can and will be used by emergency responders, whether in civilian or military use, as vividly illustrated in a recent technical report prepared by Pacific National Laboratory. [861] It is likely to find similar active polymeric surfaces or electronic skins also in structural health monitoring applications (bridges, overpasses, safety systems, etc.) [845]

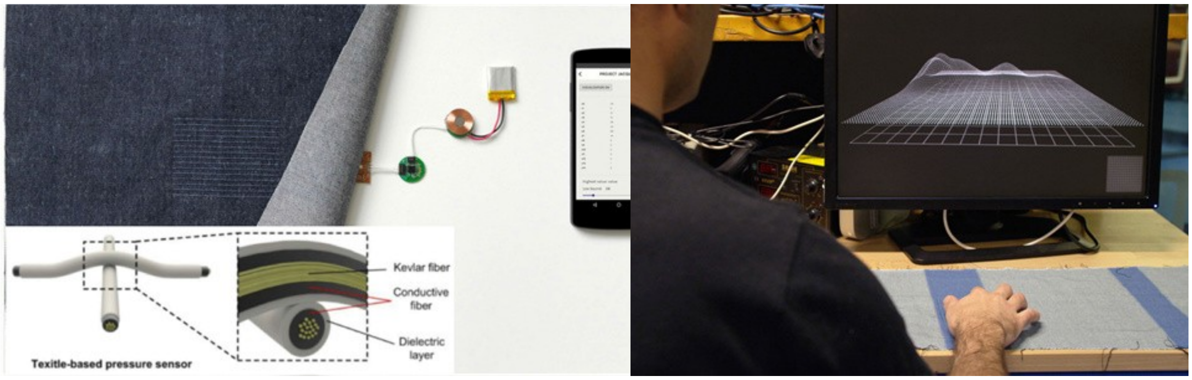


Figure 84. Google's Project Jacquard [822]

<u>TECHNOLOGY GAP: MIGRATION OF PRINTED SENSORS ONTO TEXTILE</u>

Many advanced sensors developed on flexible polymeric or paper surfaces are never implemented on or integrated with textile surfaces. Since wearable FHE systems on textiles could be the preferred solution on many defense and consumer products, there appears to be a clear need to adapt or re-implement sensor device proven to work on paper/plastic on textiles with minimal loss in flexibility and sensitivity.

<u>POTENTIAL SOLUTION</u>

On cases where simple lamination of printed sensors will not work or proximity to specific body parts is necessary, re-implementation of the sensor device using the toolset available to conductive textiles such as embroidery, weaving, or printing would be needed.

Example 4 –LCR sensors: One of the most common requirements for a given FHE system is the presence of low-cost passive sensor arrays that can transduce user input when needed and provide positional or motion feedback to the system. Based on the good sensitivity of simple passive L, C, R (inductance, capacitance, resistance) elements on a flexible surface, there are multiple ways to build and explore these types of sensors. The variety or design and material combinations is staggering, and LCR-based touch/pressure sensors constitute some of the most mature and established sensor families, especially when overlaid onto display elements to provide the ubiquitous touch screen capability. However, beyond displays, tactile/pressure sensors can be used for a broad range of functions including biochemical sensing, strain sensors, microphones, motion sensing, flow sensing, and proximity control, as well as resonators in electrical circuits. In fact, existence of a wide variety of simple yet effective passive devices for major sensing needs is one of the most important incentives for implementing a full system using FHE technology. As low-cost efficient microcontrollers that can work with such sensors in real-time are already developed for many industrial and consumer applications, large arrays of them can be readily adapted for FHE applications with minimal cost. Accordingly, for completeness, some interesting examples of passive LCR-based sensors that can be applied to FHE systems and provide context for more complex systems are described in the next few paragraphs.

<u>Piezoresistive Sensors:</u> A simple piezoresistive sensor array created by CNT-dispersed PDMS polymer layers sandwiched between two electrodes is shown in Figure 85. Produced in this case by screen-printing method, the array is dense and sensitive enough for mapping out the palm

surface. In higher densities, this type of sensor can also be used for fingerprint sensors, strain gauges, or to map out mass distributions. It is possible to replace the PDMS-CNT layer with simple ultra-thin resistors made from metallic nanoparticles of Ag or Cu, or graphene, which would mean that this basic architecture can be replicated in many material sets used in printing techniques used for FHE systems.

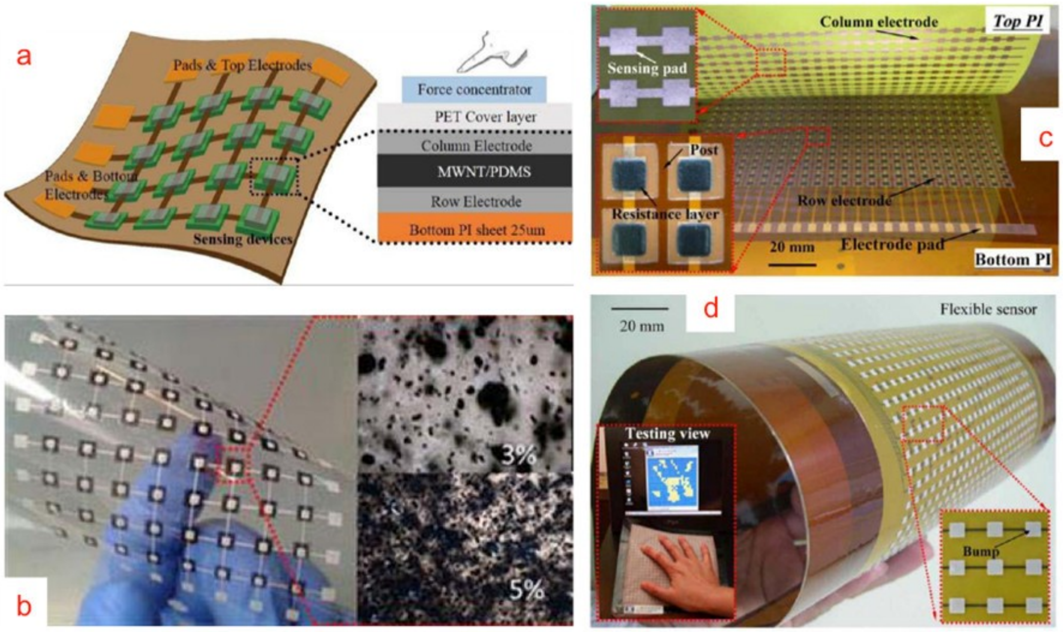


Figure 85. Simple CNT-based Piezoresistors

<u>Capacitive Sensors</u>: Since capacitive sensors are generally easier to fabricate and more practical to measure accurately in digital applications, they have found a greater acceptance in the flexible sensing community. This is because, in printed sensors, interdigitated electrode (IDE) capacitive elements are not only easier to form with air as the single dielectric, but they can also provide proximity sensitivity that is not found in piezoresistors. Besides the larger size requirements in the planar form, these sensors can be utilized for multiple purposes in a broad range of applications. In Figure 86, two example sensor architectures are illustrated: an array of capacitive sensors in a matrix arrangement for position or strain measurements, and an IDE designed for gas sensing. [850],[851] In the former case, given in Figure 86(a-e), a cross-bar capacitive arrangement is used to sense position or strain in an array. The electrodes are formed by patterning Ag nanowire solution and a dielectric tape is used as a spacer. The linearity of the capacitive sensor is noteworthy, even at 60% strain. In the case of the IDE example of Figure 86(g-h), an inkjet printed Ag nanoink is used to define the capacitor sensor with ~100 μm spacing, and the surface is passivated with polyether urethane (PEUT) to provide stable measurements over wide temperature and humidity conditions.

<u>Inductive Sensors</u>: Inductive sensors can be fabricated and operated with very similar approaches as those used for capacitive elements. However, due to their purely planar nature, these devices tend to be larger in size and more difficult to contact. As a result, capacitive sensors are often preferred and inductive sensors are reserved for approaches that require high-quality proximity sensing that is associated with the out-of-plane magnetic field component resulting from their 2D

geometry. Also, inductive sensing can be used for sensing magnetic elements and media as well as in applications where LC resonant circuits are required for higher quality factor (Q) resonant response. In particular, in electronic textile applications on which skin-contact may not be guaranteed, using inductors for sensing has advantages. Such sensors are commonly used in biomedical applications such as blood pressure and heartbeat sensing.

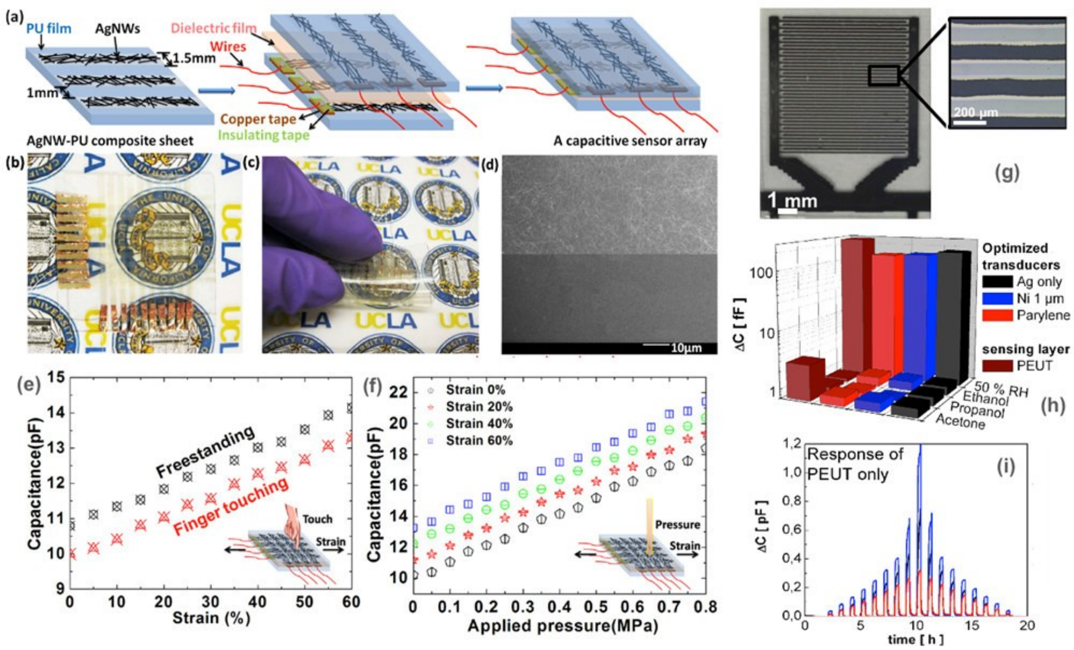


Figure 86. Printed Capacitive Elements: (a-f) Position/Strain Sensor Arrays [865], (g-i) Passivated Gas Sensor [850]

Example 5 – RF Sensors: Despite the higher loss of most organic materials and substrates at high frequencies, printed RF sensors can have significant impact on FHE applications. Both passive and active RF devices and RFID elements can be included in this class of sensors. [835, 866] Contrary to organic devices, RF sensors typically come in simpler structures and larger sizes depending on the frequency of operation. They can be directly printed using conductive inks of metal nanoparticles and/or carbon nanostructures (nanotubes or graphene). RF sensors are very susceptible to electro-magnetic waves. Environmental factors can lead to significant changes that cause RF emission, propagation, coupling, or scattering in planar devices. Therefore there is a large collection of devices, both active and passive, that can be used as sensors. Several prominent examples will be provided in this section.

In passive operation, a port parameter (impedance, power reflection, or transmission) is monitored in real time using an RF signal source coupled to the system via an antenna or fed into the sensor via an input terminal, as shown in Figure 87(a).

In this case, the RF sensor is composed of a CNT film that shows large sensitivity to the presence of ammonia (NH3) gas and is embedded into a passive RFID tag architecture. The measured power reflection changes more than 10 dB at its resonant condition after exposure to NH3. This concept can be expanded to higher frequencies by incorporating the sensitive film into antenna structures, such as the patch antenna shown in Figure 87(b) which has a resonance at ~6.8 GHz that shifts to

lower frequencies as the ammonia concentration rises. This type of active embedding of RF sensors can turn any given antenna pair into a wireless sensor, which would be of great interest to FHE systems within an existing wireless infrastructure.

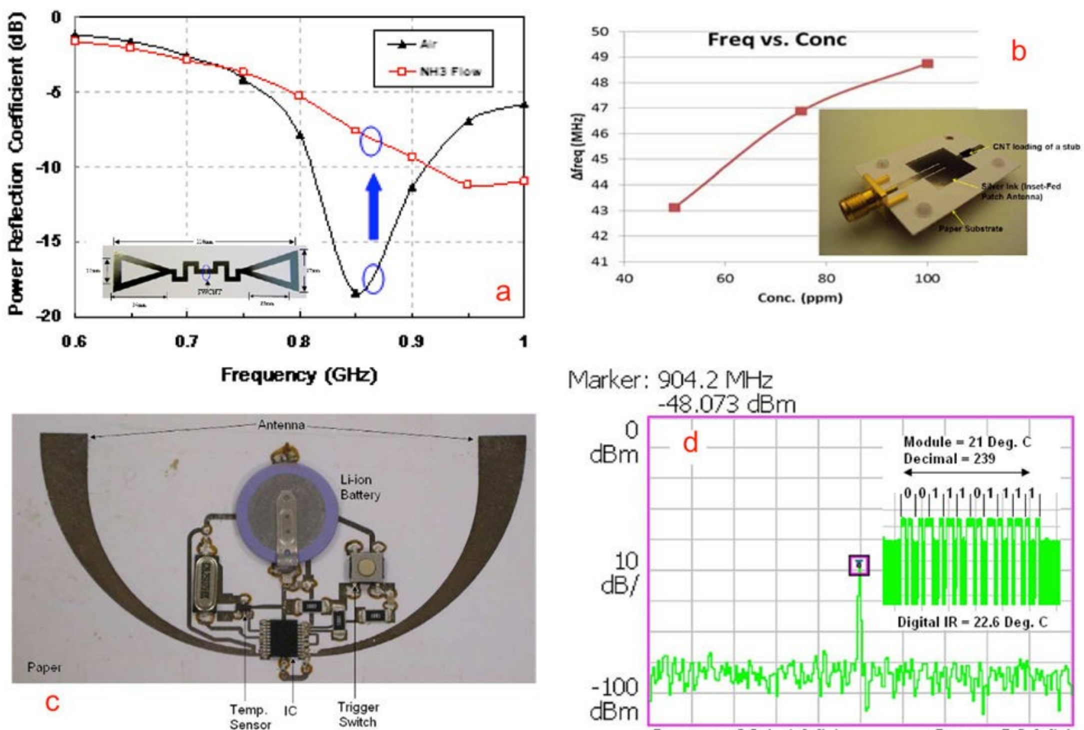


Figure 87. RF Sensors Embedded in (a) Passive and (b-c) Active RFID Tags [838]

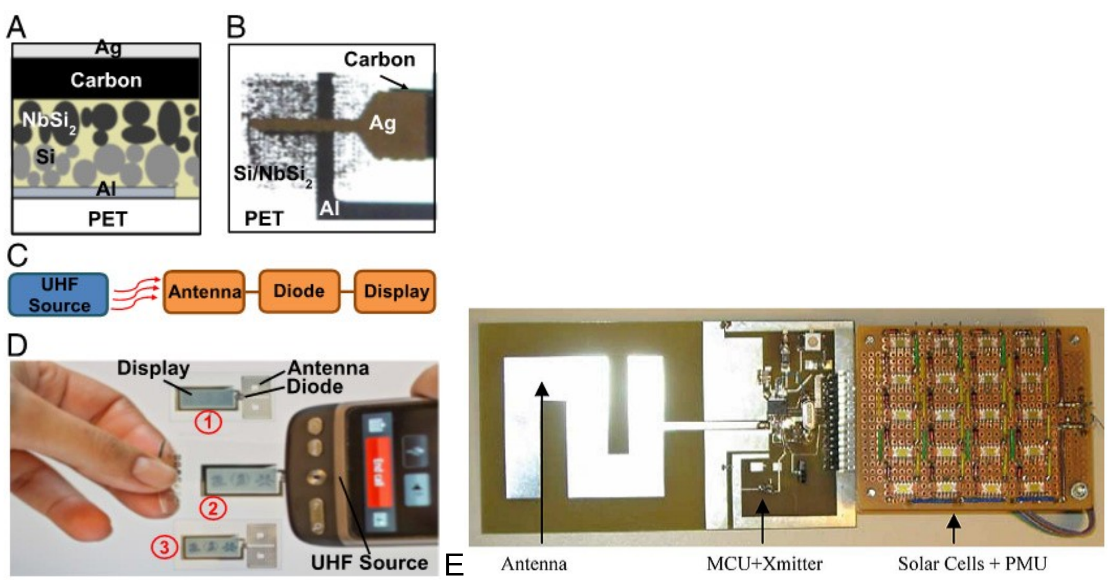


Figure 88. Primitive FHE Systems (A-D) with Built-in RF Sensing & Display Elements &

(E) Solar Powered RF-Antenna
As seen in Figure 87(c-d), a complete battery-operated active RFID can be built using this principle and can be considered a simplistic FHE system. As a matter of fact, all active RFID systems are essentially simplified FHE systems if they are built on flexible substrates. Therefore, RF sensors embedded in active and passive flexible RFID hosts can constitute one of the essential building blocks of primitive FHE systems as they become fully developed and expand into fully-fledged versions, as shown in Figure 88. In this figure, two additional complete RF systems with built-in sensors and devices are shown. In the first case, printed diodes are used as energy harvesters integrated into an RF antenna that is used to power simple displays for active information using RF ambient energy. Figure 88 (e) shows a second example, a simple FHE system with an RF wireless link and integrated solar harvester that powers it. Although no sensor is included in this case, it is trivial to adapt a given RF sensor in this prototype system, either with the antenna or the transmitter end.

TECHNOLOGY GAP: SENSOR ENRICHED ACTIVE RFIDS

All active RFIDs can be considered to be the primitive FHE systems if their capabilities are further extended with the addition of necessary low-power sensors. This would not only close the gap between the two definitions, it would also help FHE assume a greater context, more applications, and a broader marketplace, along with the expertise in building and using the RFID toolset.

POTENTIAL SOLUTION

Besides technical issues of integration and low-power design, part of the solution is also perception and training: active RFIDs must be introduced, recognized, and designed as simple FHE systems by adapting more sensors and printed/transferred IC components within their architecture.

Example 6 – Packaging: Disposable, organic based sensors composed of paper based materials are currently used in food packaging and related areas. Single use sensors with thermochromics ink are available to determine the temperature of cooked food. Oxygen sensors with color indicators are used in food packages to determine freshness. [867] Packaging sensors used for food health and safety purposes are most often comprised of paper materials which enable packaging recycling at the end of their life. [843] Disposable flexible sensors are also widely dispersed in the pharmaceutical supply chain, again for sensing temperature, humidity and other environmental factors. Smart blister packaging for medication from Information Mediary Corp. (Ottawa, Canada) uses a printed sensor grid on polymer or paper label substrates for monitoring patient medicine compliance. When the package is perforated by the user, data is stored or sent to any near-field communication or Bluetooth device. [868] Qolpac (Amsterdam, Netherlands) makes similar smart blister packaging, which can also alert patients and caregivers if a medication dose has been missed. [869]

Figure 89. Qolpac Smart Blister Package (left) [869] & Transdermal Alcohol Sensing Device (right) [870]

7.3.10. Power

The necessity of uninterrupted power for modern conveniences and the impact of energy sources on the economy of modern societies are not new phenomena. The surge of portable electronics and wireless connectivity in the new century have made these socio-economic realities all the more personal and immediate. This is best epitomized by the use of smart phones that are not just communication devices anymore, but have evolved into digital hubs that essentially combine a personal assistant, a reading aid, a wallet, an entertainment source, and a canvas for artistic and social expression into one device. Since people can no longer consider professional or private life without uninterrupted use of smart phones, future FHE systems that are likely to execute important functions will have to operate by taking advantage of all energy resources so they can operate non- obtrusively and without interruption. Therefore, the power problem has two aspects as it relates to FHE systems. First, FHE systems must operate independently and remain free of all wired attachments and weight associated with power supplies, or minimize their usage as necessary. This means that FHE systems should take, and so far have, a pragmatic approach of developing an entire power ecosystem on flexible substrates to harvest energy from all possible ambient energy sources, as indicated in Figure 90. This will not only help FHE systems, but will also benefit conventional portable electronics and handheld devices. [871] The secondary, more implicit, but perhaps broader issue, is that FHE systems could be the one and only practical system that can combine all unique developments in power devices (high-capacity and compact batteries, super capacitors, organic solar cells, and energy harvesters), into a single technological platform efficiently and affordably. Beyond FHE, such a platform will be of interest to most electronic designs where 'green' solutions are needed or power independence will be beneficial. Consequently, it is possible to view the device examples given below in two lights: solutions to power FHE systems, and creation of 'hybrid green' power ecosystem.

Energy-Harvesting Sources Today

Energy Source	Characteristics	Efficiency	Harvested Power
Light	Outdoor Indoor	10~24%	100 mW/cm^2 100 μW/cm^2
Thermal	Human Industrial	~0.1% ~3%	60 μW/cm^2 ~1-10 mW/cm^2
Vibration	~Hz–human ~kHz–machines	25~50%	~4 μW/cm^3 ~800 μW/cm^3
RF	GSM 900 MHz WiFi	~50%	0.1 μW/cm^2 0.001 μW/cm^2

Courtesy of Texas Instruments

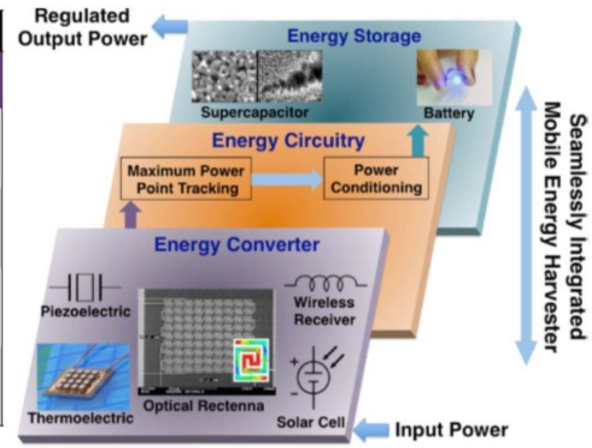


Figure 90. Harvestable Ambient Energy Streams (left) & Typical Integrated Energy Infrastructure (right) [703, 872]

At the present time, the examples that follow belong to a class of single devices that work in isolation and are still under development. In some cases, such as solar cells, the performance is not totally impressive. However, when combined on the same substrate and further developed, these devices can pack significant power or prolong operational periods remarkably such that the need to recharge via external sources can be minimized. In any case, the trends and expectations dictate that FHE systems become more compact and be designed for ultra-low power operation so that even minute energy sources can help operational endurance and longevity.

The following sections only provide several examples in each category, in what is otherwise a very broad field, and keep the focus on FHE system applications as opposed to the broader implications indicated above. The important pragmatic take away message is that there is sufficient expertise to generate 1mW to 10mW power needed for practical FHE implementations using various device combinations. If and when the power levels reach 100mW and beyond, it may be possible to build 'hybrid green" power modules that can become the 'killer' application that alone can reward FHE investments, while also accelerating FHE development, since more can be done as the power levels and time between re-charging intervals increase.

TECHNOLOGY GAP: INTEGRATION OF ENERGY HARVESTERS

Many examples of flexible energy harvesting devices that exist are designed for a single source and a unique set of operational conditions in isolation. It is crucial for FHEs success, especially in the demanding and service-critical defense applications, to harvest all ambient energy sources in an integrated and smart fashion.

POTENTIAL SOLUTION

A combination of all available energy harvesting sources (solar, thermal, vibrational, RF/microwave) as well as the use of on-board (artificial) intelligence to maximize harvesting strategies along with balancing of storage tools such as batteries and supercapacitors behind a single power managing chipset is needed to truly 'power' independent FHE products, including active RFIDs that can gain most from harvesting in the short run. Higher levels of harvested power (≥ 100mW) may enable 'hybrid green" power modules that can become the 'killer' application that starts to reward FHE investments.

7.3.10.1. Energy Harvesting Devices

Energy harvesting from ambient sources (other than light) such as vibration, pressure, heat, and friction are important for FHE systems, since they may be situated at locations that do not receive sufficient light and are exposed to large levels of other forms of energy that otherwise would be wasted. For example, energy harvesting can be accomplished where two large surfaces exist that have distinct ambient conditions and that energetically are very different, such as wings of drones, engine parts, or gas/oil pipelines. Very different energy conversion methods and devices are implied in each case, and some are easier than others. As a result, there are many different approaches and material/device combinations utilized in energy harvesting systems. Typically, for thermal conversion, thermoelectric devices exploiting Seeback effect in thin films that have large Z-factors are employed. For friction and vibration, piezoelectric layers of ZnO or lead zirconate titanate (PZT) ceramics or textured polymer/textile surfaces that contain triboelectric generators, or pre-packaged MEMS resonating harvesting systems can be used.

To illustrate the concept behind energy harvesting via friction, a triboelectric nanogenerator (TENG) is shown in Figure 91 which converts mechanical energy into electric energy via electrostatic induction and contact electrification. In a TENG, charge transfer occurs between two surfaces (Ni anode vs. Parylene cathode) that generates static electricity when deformed or subjected to friction. The Ni layer is also used as the conductor that completes the circuit to the external load, as seen in Figure 91(a). In this example, the electrodes are shaped into woven fabrics using flexible polyester threads that were coated with conductive layers, as indicated in Figure 91(b). The transfer of electrons from the positive Ni film to the negative Parylene film occurs when the two electrodes come close to each other when they are pressed. It is also possible to design a more effective generator by coupling several TENGs to one another and separating them using additional insulator layers. [873] The tests on different motions have shown that TENG fabrics worn under the foot, arm, and near the elbow can all utilize different types of motions and generate charge at varying levels. [873, 874]

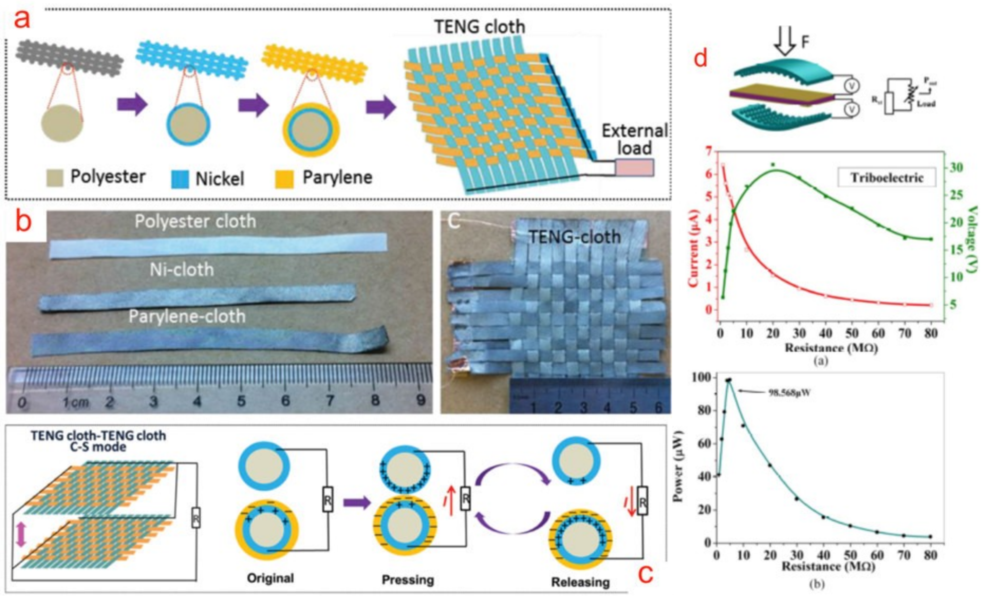


Figure 91. Triboelectric Nanogenerators: (a) Principle; (b) Practical Example; (c) Coupled Operation; (d) Utilization of Nanofiber Mat to Improve Efficiency

Using other flexible, printable materials, it is possible to improve the performance of TENGs, as explored by Wang et al. [874] To enhance the efficiency of static electricity induction, they utilized piezoelectric PVDF-TrFe polymers that are electrospun into highly polarizable nanofiber mats that also maximize friction. The other flexible friction layer is a PDMS layer doped with multiwall carbon nanotubes. PDMS has very good flexibility and deformation and therefore is a good option to be used for TENG. The result is a combination piezoelectric–triboelectric generator that is very efficient and capable of harvesting mechanical energy to charge electric polarization across coupled electrodes up to 21V with a power of ~100 µW under a 5MΩ load. [874] This is a modest power level, but many TENG designs are still in their infancy.

Optimization of material choices and use of multilayer techniques can drive the power level up to the ~1mW level which is sufficient to power sensors and RFID circuitry in burst mode. Moreover, depending on the operating medium (humidity or ionic plasmas), surface area, and application context, TENG efficiency can reach acceptable levels for certain applications, all based on the simple motion of limbs.

Application Examples: Despite the limited power they have, the unique nature of piezoelectric harvesters make them ideally suited for a number of specific applications that have just the right power level or the form factor. These are briefly summarized below.

Biomedical Device- Piezoelectric materials will serve as a key enabling technology for a wide number of flexible hybrid devices. Implanted medical devices such as cardiac pacemakers, cardioverter-defibrillators, cardiac monitors, and others must be surgically removed in order to replace depleted batteries. Flexible piezoelectric generators based on PVDF and powered by blood flow have been studied in vitro and in vivo to determine the feasibility of powering implantable medical devices currently powered by batteries. [876] Other work has used respiratory motions to power an implantable flexible pacemaker. [877]

Wearables- Significant research has also been conducted on flexible piezoelectric wearable generators, such as shoe inserts [878, 879] and woven textiles. [880] The devices are ideally suited to power portable electronic devices instead of batteries. Large-scale fabrics with piezoelectric fibers could serve as portable power generators harvesting energy from wind. Prototype or commercially available flexible sensors to measure pressure, [881] strain, [882] force, [883] temperature, [884] and other sensing applications have been demonstrated.

Piezoelectric generators could provide lifetime power for flexible biosensors and numerous other wearable devices. Remote and wireless sensors could be powered with energy created from a piezoelectric generator and stored in a flexible battery or supercapacitor.

Sensors- Researchers at Nokia have created a flexible and transparent touch screen sensor using PVDF piezoelectric material. [885] Samsung envisions piezoelectric technologies will enable future self-powered touch screen sensors and wearable artificial skins. [886] Traditional piezoelectric devices are used as actuators, microfluidic pumps, spark generators, accelerometers, and in a variety of other applications. Flexible piezoelectric devices can certainly replace the rigid counterparts assuming the economics and design are beneficial.

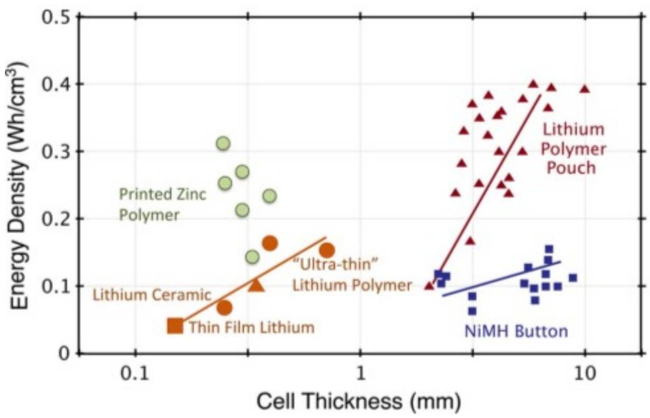
Smart Textiles- Meggitt A/S is a manufacturer of piezoelectric materials, components and devices based in Denmark. Recent work has focused on smart textiles for everyday clothing or specialized working gear. Meggitt intends to replace mostly passive piezoelectric smart textiles with more active devices such as motion, carbon monoxide, temperature, and other piezoelectric based sensors. [887] Examples include lab coats with specific chemical sensors and alert systems for the wearer, protective clothing for firefighters (that include piezoelectric biosensors), and consumer clothing for exercise and health monitoring. Smart textiles for soldiers are also envisioned. Meggitt researchers cite several challenges for low cost, large scale manufacturing of flexible piezoelectric integrated clothing including compatibility with flexible materials/fabrics, compatibility with commercial printing techniques (e.g. pad, screen, and ink-jet printing), low processing temperatures, and the reliability and ability to withstand repeated washing and wearing. Meggitt has also developed PiezoPaint™, a lightweight, flexible piezomaterial that can be directly printed on nearly any substrate.

7.3.10.2. Polymer Batteries

	Lithium Ceramic Composite and Thin Film Lithium	Thin Zinc Carbon Primary	Lithium Polymer Pouch Cell	Printed Zinc Polymer
Format	Flex PCB laminate and semi rigid thin PCB and coated films	Assembled separator + printed components in sealaed pouch laminate	Assembled electrolyte separators and electrodes in vacuum selaed pouch cell	Fully printed cell stack with laminated packaging
Energy Density in Thin Format	<50 – 150 Wh/L	<50–150 Wh/L	100 - 200 Wh/L	100 - 300 Wh/L
Cycle Life	>500 cycles	1	>500 cycles	200 cycles
Pulse Capability	3C - 10C	C/3 to C/20	1 to 5C	5 to 10C
Flexibility	Poor for vacuum deposited cells. OK for ceramic composite cells	Poor to Fair. Package buckling an issue in some designs	Poor. Packaging failure, gas expansion and electrical failure.	Good. Monolithic, flexible polymer-based structure.
Safety	Fair. Reduced leakage and expansion versus lithium polymer cells. Lithium	Good. Low toxicity and low reactivity anode and cathode materials.	Poor. Flammability, reactivity, disposal concerns	Good. Low toxicity, low volatility electrolyte and low reactivity anode and cathode materials.

Figure 92. Comparison of Thin-Film Polymer Battery Technologies [796]

Steady advances in forming thin-film electrodes and polymer based Li-ion and Zinc electrolytes that can be deposited and assembled together using essentially the same toolset as printed electronic sensors and transistors have made ultra-thin, low-cost, and scalable battery elements available to FHE platforms. Current *Zn-polymer* based batteries satisfy all requirements for packaging and flexible operation, exceeding the capacity of Li counterparts with a superior pulsed performance and reduced thickness, as can be seen in Figure 92 and Figure 93. [796, 888] This has two significant implications. First, having a low-cost ultrathin battery technology with the same flexible characteristics as the flexible device or sensor elements, is an extremely powerful argument for migration to FHE products. This is to say that FHE designs may be preferred against conventional portable systems as a result of convenient battery technology increasing its market penetration. Second, the battery technology itself can be marketed in more conventional formats and applications (i.e., the general battery market), which can enhance financial strength and market depth for FHE technologies. In other words, just like energy harvesting 'green hybrid' systems, batteries developed in the context of FHE systems can end up in general markets, which would mean financial competitiveness for companies investing in flexible technologies as a whole. Much like the solar devices to be argued next, with the help of FHE systems, battery technology could get a renewed acceleration and new perspectives for the much needed 'dramatic jump' in performance and charging speed, which has long eluded bulk materials. Hence, there is yet another symbiotic relationship between battery and FHE technologies. Each one needs the other one to make a stronger market case, and the sum could be much bigger than the parts. Several examples of flexible, ultra-thin batteries are used in this subsection to explain how FHE systems may utilize them and what type of trends are expected to impact flexible battery technology development.



Specification	Application Target	Flexible Battery State of the Art
Area	2 to 100 cm²	<1 to 50 cm²
Capacity	10 to 100 mAh	1 – 5 mAh/cm² depending on rate
Pulse Currents	≥ 1C ; 10 to 100 mA in ≤10 cm² cell	Up to 10C; >20 mA/ cm²
Sustained Currents	0.1 to 10 mA	Up to 20C, 20 mA/cm2
Flexibility	≥ 13 to 25 mm radius 1000 cycles	≥ 13mm radius >2000 cycles
Shelf Life/Charge Retention	3 to 12 months	>9 months
Thickness	≤ 1 mm, Preferably <500 µm	300 to 400 µm

(a) (b)

Figure 93. (a) Polymer Battery Energy Densities vs. Thickness; (b) General Characteristics of Flexible Batteries [796]

Flexible Lithium Ion Batteries: Conventional lithium ion batteries are made of a carbon anode and a lithium metal oxide cathode, such as LiCoO2, LMnO or similar. The electrodes are separated by a polymer layer and an organic liquid electrolyte and solvents fill the package and provide charge transport. [889] Typically ionic liquids based on lithium hexafluorophosphate (LiPF6) are used as electrolyte. [890] Nanostructured carbon materials like CNTs and graphene have been added as anodic materials in recent research.

For flexible lithium ion batteries, the key-enabling component is a flexible solid-state electrolyte. [891] Polymer electrolytes and solid gels provide better reliability and safety and allow for larger design and size options for flexible batteries. Gel polymer electrolytes (GPEs) have been studied extensively because of their low toxicity, high ionic conductivity, low flammability, and low leakage. [892 - 898] Mechanical strength of the electrolyte-impregnated polymer has posed issues, and some researchers have developed advanced acrylate polymers, which show high strength and flexibility when used in conjunction with LiPF6 electrolytes. [899] Complementary work has shown that Al2O3 nanoparticles in place of the polymer matrix results in a bendable and conformable composite type GPE. [897, 899] A second class of solid-state electrolytes known as plastic crystal electrolytes (PCEs) have the same benefits as GPEs but without great flexibility. CPEs research has focused on improving PCE mechanical properties by incorporating a polymer matrix as a backbone. [894, 900]

Carbon-based Nanomaterials: A vast number of groups are also researching carbon-based nanomaterials for flexible battery electrodes. These include CNTs, graphene, carbon-based textiles/cloth, and cellulosic, paper-like materials. [891] CNTs have excellent mechanical and electrical properties and there are a variety of processing methods to assemble flexible CNT membranes. The advantages of using CNTs for flexible electrodes are numerous, including weight reduction, strength and resiliency for flexible devices, improved electrokinetics due to fast electron/ion transport in the CNT network, extended cyclic stability by accommodating active material volume change, and easy dispersion of active material. For example, vacuum filtrated CNTs have been used as stand-alone anodes [901 - 903] demonstrating flexibility and capacities up to 550mA·h·g-1. CNTs vacuum filtered directly onto the battery separator

membrane have improved mechanical properties over standalone films with no reduction in capacity. [904]

Still more work has focused on CNT composite anodes based on chemical vapor deposition (CVD) fabrication techniques. CNTs have been grown on conductive carbon papers, [905] carbon fiber membranes, [904] graphene paper, [906] and PVDF composites. [907] These anodes showed higher capacity than other free standing CNT based films due to the large surface of CVD grown aligned nanotubes. Flexibility and mechanical strength of these CNT anodes are also improved because of the substrate papers, which are able to withstand the CVD environment. Performance of the composite CNT type anodes again show capacities up to 265mA·h·g-1 for aligned CNTs on PVDF substrates and up to 546mA·h·g-1 on carbon fiber paper. CNTs grown directly via CVD into anode structures have a higher purity than the vacuum filtered CNT anodes, which contain surfactant impurities as a consequence of processing.

Other materials such as silicon, germanium, tin and transition metal oxides have been researched as anode materials due to their extremely high capacities. However, these materials suffer from destructive effects during power cycling, significantly degrading after a few cycles. [908, 909] In attempts to increase the cyclability of anodes and utilize the higher capacity materials in flexible configurations, CNTs have been investigated as a matrix materials for composite metalloid/CNT anodes. [891] Fe_3O_4/CNT composite electrodes fabricated with vacuum filtration techniques were used to create flexible anodes with capacity as high as 1000mA·h·g-1. [910] A method using aerosol sprayed Fe_3O_4 nanocrystals in conjunction with vacuum filtration CNT matrix integration resulted in a similarly high capacity. [911] TiO_2, SnO_2, and Si have also been investigated in combination with vacuum filtered CNT architectures, but with less promising results. [890] Other methods, such as CVD and dry-drawing CNT processing have also been used with metal nanoparticles (Fe_2O_3, Cu_2O, SnO_2, MnO_x, Si, etc.) to create flexible anodes considered to be promising candidates for use in lithium ion batteries.

Nanomaterial-based Electrodes: Research around CNTs for cathode materials in lithium ion batteries also has a broad scope. CNT cathodes with $Na_xV_2O_5$ show a 20-60% increase in capacity over traditional Al foil/ $Na_xV_2O_5$ cathodes. The CNT cathode shows good electron and ion transport, high structural integrity, and suffers from no oxidation as can be the case with Al foil based cathodes. [912] Additional work is being performed with lithium trivanadate (LiV_3O_8), [913] V_2O_5 nanomaterials, [914] as well as traditional cathode materials such as $LiCoO_2$, $LiMn_2O_4$, etc. [891]

Graphene and graphene based materials, such as graphene oxide, have also seen a significant amount of research for use in flexible battery electrodes. Its high electrical conductivity, chemical stability, and mechanical flexibility coupled with low cost, large area production methods are an attractive alternative to other flexible battery materials. [915] The incredibly high surface area of graphene can theoretically provide higher energy storage than CNTs, and stacked sheets easily allow for better electrolytic ion diffusion. [916] Furthermore, fewer impurities result when processing graphene materials, lending it another advantage over CNTs. [843]

The earliest graphene based anode was fabricated with vacuum filtration methods similar to CNT based anodes [917], resulting in graphene papers. While displaying good mechanical and

electrical properties, this graphene anode had a relatively low capacity of 84 mA·h·g-1, possibly due to agglomeration of graphene flakes during drying which inhibits electrolyte transport. Dispersing CNTs among the graphene reduces agglomeration and results in higher capacities with greater cyclability. [918] Other methods of creating graphene papers with optimal porosity for electrolyte transport such as photoflash and laser reducing, [919] and ultrasonication plus acid oxidation [920] have also been explored in order to increase capacity and rate capability for the electrodes. CVD methods for directly producing graphene anodes have also been reported. One such example is a solid state flexible battery fabricated by Nokia researchers with an anode of graphene on Cu foil, a cathode of Li and a solid polymer electrolyte. The device is 50µm thick, fully flexible, and capable of powering an LED. Graphene aerogel sheets produced by CVD and pressed into a wrinkled sheet resulted in an anode with a capacity of 864 mA·h·g-1 and good cycle performance. [921]

Cathodes based on graphene have also seen considerable interest. Cathodes such as iron trifluoride (FeF3)/graphene paper [922] and V2O5 incorporated graphene paper [923] have shown promising results as flexible current collector, without the drawbacks of conventional Al foil based electrodes.

Research involving flexible thin-film battery technologies can be largely separated into three categories: (1) novel flexible packing design for existing polymer-based Li and Zn batteries; (2) novel and efficient laminated electrode or electrolyte designs; and (3) designs that use printing methods to establish novel battery solutions. Figure 94 shows various examples of novel packaging formats that are crucial for adaptation of existing polymer based batteries, including aluminum pouch (a), tubular cable format (b), flexible PDMS capsules (c), and stretchable bands (d); and laminated paper with ultrathin carbon nanotube (CNT) electrodes (e-g). These techniques are not necessarily mutually exclusive and can be combined in some cases, as in a case that uses CNT or graphene ultra-thin electrodes to replace more expensive Au/Ag electrodes. Each of these batteries have confirmed flexible operation under repetitive stress and hundreds of charge/discharge cycles.

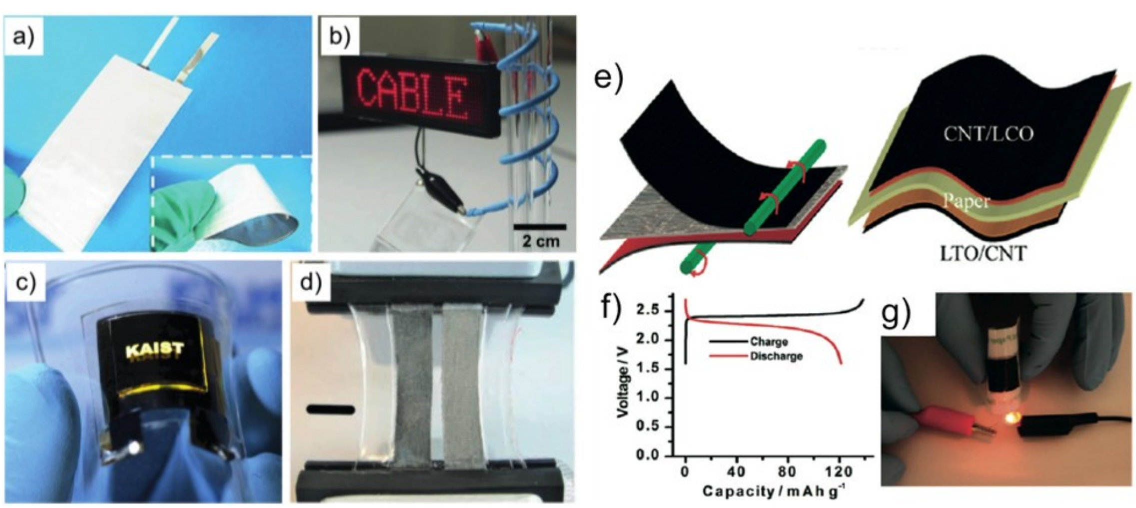


Figure 94. Various Flexible/Nano Battery Examples [924]

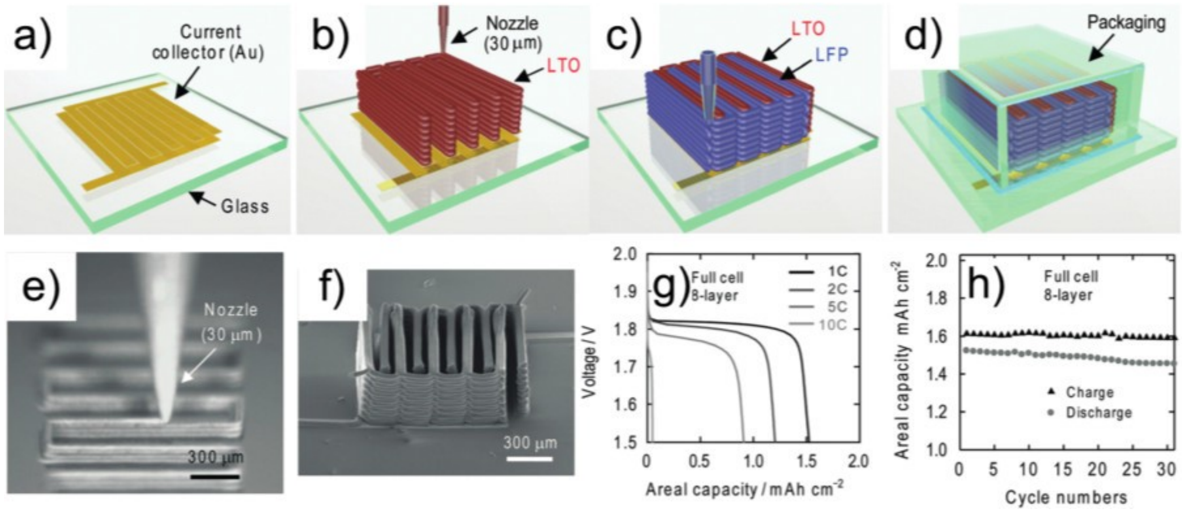


Figure 95. Directly Printed PDMS Encapsulated Liquid Battery Cell [925]

Another example of a flexible battery is provided in Figure 95, where direct writing of battery elements using high-resolution 3D additive printing via a capillary device is used to form the battery. In this case, multiple layers of the battery can be stacked together, which increases capacity and saves space. The final Li-ion based battery device, which also uses a fluidic electrolyte mixture, is encapsulated with a PDMS gasket that isolates it from all ambient elements while also providing sufficient flexibility. Because of its multiple layers and liquid electrolyte, this battery outperforms many conventional and flexible counterparts for energy density and can support the same currents at different standard capacity (C) rates and multiple charge-recharge cycles.

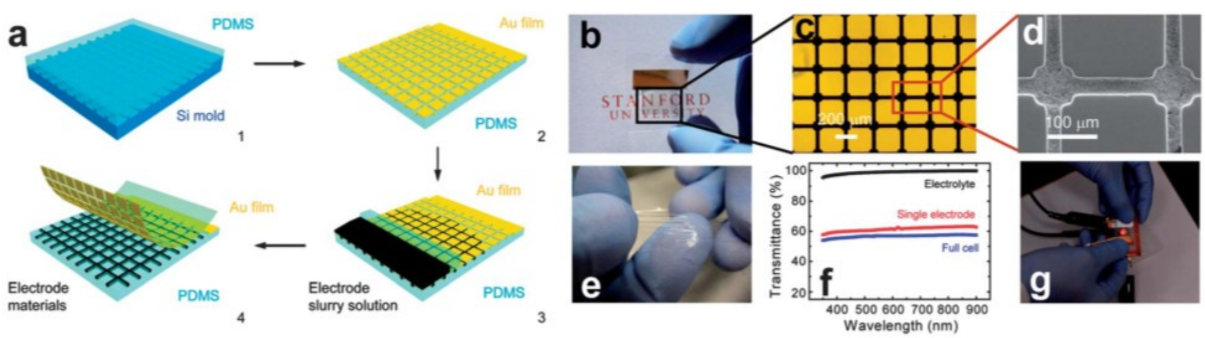


Figure 96. PDMS Mesh-based Stretchable Ultra-Light Transparent Battery Cell [888]

To illustrate the opportunities offered by flexible technology and printing processes for battery research, Figure 96 shows a unique effort: a 60% transparent battery based on PDMS grid structure built using a common micro-fluidic casting approach. The micro channels were filled with active gel electrolytes in a high-resolution grid that evades human perception. Besides holding the gel electrolyte, the PDMS grid also provides high flexibility and transparency for this design and can hold 80% of its fresh capacity after many cycles. It is possible to extend these novel battery examples even further as stretchable batteries that have very high resistance to deformation, as shown in Figure 97. That design utilizes Zn/MnO2 battery technology on various stretchable fabrics or transparent conductors formed by silver nanoparticles and nanorods. In various forms, under stretching or bending deformations with strain levels reaching 150% or

under 90% twisting, this battery system works well and is reliable. This is good news for wearable technologies and physical environments where solid batteries cannot operate.

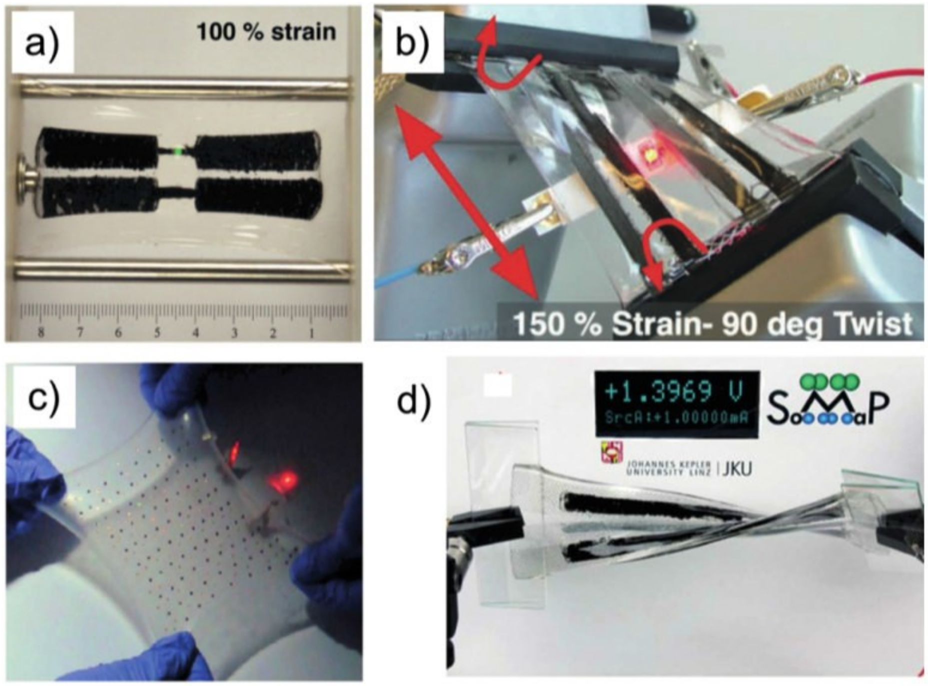


Figure 97. Various Deformations of Zn/MnO2 Stretchable Batteries [925]

Battery Examples in Production: Samsung introduced a flexible battery in late 2014, which it intends to include in its wearable electronics products such as smart watches and fitness bands. [926] No timeline for production has been determined, but it will take at least 'a few years' to overcome safety, reliability and manufacturing hurdles. Samsung has already included a curved (but mostly rigid) battery in their consumer product 'Gear Fit' smart band. Other large companies such as Apple, Nokia, Showa Denko, and NEC are carrying out basic research and development of flexible batteries as well. [927]

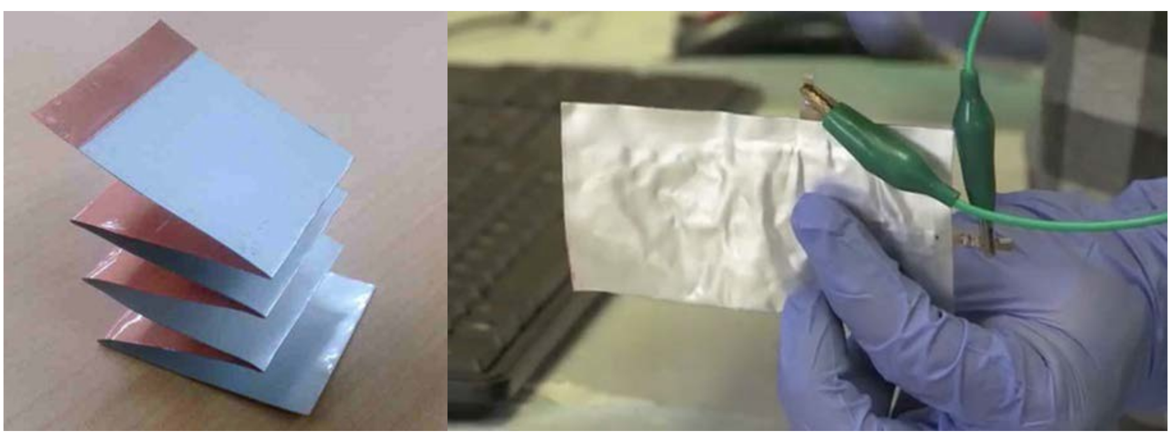


Figure 98. Foldable Flexible Battery Prototypes from Showa Denko (left) [928] & Stanford University [929]

In late 2014, Nokia was issued a patent on a self-charging, graphene-based, flexible photon battery. [928] The device is designed to regenerate power through continuous chemical reactions from humidity in air. It remains unclear whether Nokia intends to prototype or develop the technology beyond patent. This is in addition to previous work that Nokia has performed on flexible and printable lithium ion battery electrodes utilizing graphene nanoplatelets modified with TiO_2. [931]

Showa Denko Packaging Co. unveiled a prototype flexible Li battery in earlier 2015 that utilizes a conductive polymer laminated package, which allows a direct connection to the battery electrode. [932] The packages are aluminum based, and result in a 50% reduction in thickness for ultra-thin flexible batteries. The battery, Figure 98, is approximately 100µm thick and can be folded numerous times, giving it almost infinite form factor options for end use device design. Stanford University researchers have developed a prototype aluminum ion battery with a 70 $mA \cdot h \cdot g^{-1}$ capacity and a discharge voltage of ~2V. [933] It has a current density of about $3000 W \cdot kg^{-1}$ and is able to charge/discharge 7500 times without decay. Most remarkably, it takes a little over a minute to recharge. Previous attempts at aluminum ion batteries suffered from poor performance, cathode material decay, and short life span, but the new research has solved these issues by utilizing a foamed, graphitic cathode in combination with an aluminum anode and an ionic liquid electrolyte. This battery is non-flammable like lithium ion batteries, but cannot yet power larger devices like laptops. Figure 98 shows one of the prototype batteries.

Researchers at Arizona State University have used a concept known as 'kirigami' to produce stretchable lithium ion batteries. [934] The kirigami technique involves origami techniques in combination with cutting techniques to produce an elastically stretchable/flexible form factor. The kirigami battery uses standard lithium ion processing methods and packaging, and is compatible with direct printing and similar fabrication techniques. The kirigami batteries have similar performances as standard lithium ion batteries (since the materials are essentially the same) and were able to adequately power a Samsung Gear 2 smartwatch while being mechanically deformed.

Ultra-thin, flexible batteries are currently produced by companies such as STMicroelectronics, Solicore, Blue Spark Technologies, PL Energy, PD Battery and several others. These devices generally have capacities ranging up to ~60mAh at 1.5 – 3.0V and are 750µm or thinner. Front Edge Technology, Inc. produces began production in 2009 on 50µm thick ultra-thin Nano-Energy® batteries for smart card applications, with an annual capacity of 200,000 units. [935] These devices are based on solid-state thin films using Lithium Phosphorus Oxynitride (LiPON) solid electrolyte with $LiCoO_2$ cathodes and Lithium anodes. [936] These ultra-thin batteries are 50µm thick, have fast charging time and exhibit less than 10% capacity loss over 1000 cycles. STMicroelectronics offers a 220µ thick battery with the same materials, offering similar performance. [937]

Challenges: Despite all of these advances, the large scale manufacture of safe, reliable, flexible high energy density devices still faces many hurdles. Carbonaceous materials will certainly be featured in many future flexible batteries because of their excellent combination of mechanical and electrical properties, low cost, chemical stability, and low weight. Solid-state electrolytes are also likely to play a key role in flexible batteries because of the reduced risk of combustion

compared to liquid organic electrolytes. Packaging materials needed to protect devices from the external environment while providing flexibility are another critical component. Other considerations based on application, such as optical transparency or stretchability may also be required. Compounding these challenges is the desire for rapid, low-cost production methods such as ink-jet, screen-printing and others, resulting a formidable challenge.

Applications: Much like flexible PV and displays, the applications for flexible batteries are generally obvious: providing power to devices. Small footprint devices, such as disposable chemical or biological sensors will likely incorporate non-rechargeable, ultra-thin batteries. The appeal for flexible batteries in larger devices with higher power consumption will be driven by design flexibility, weight reduction and increased power from flexible batteries.

Wearable devices- As more devices become wearable, mobile, or flexible, advanced flexible batteries will power these devices. Smaller cable-type or textile compatible batteries could potentially be woven into clothing or backpacks, reducing the overall load that a soldier might carry.

Smart card devices- Many credit cards, identification cards, transit passes, smart RFID labels and tags, and similar pocket sized cards require on board power to broadcast RFID and enable encryption or security features like one time passwords and a real time clock. Some smart cards have onboard microprocessors or memory chips. Ultra-thin, flexible batteries provide smart cards with a self-contained energy source, which enables these features. [938] E-paper devices are targeted for integration with flexible batteries, with many prototypes already seen. [939]

Biomedical devices- Consumer available, wearable biosensor devices, like fitness bands, generally use rigid, rechargeable batteries. Flexible batteries can be integrated within the strap to reduce weight and improve comfort. Similarly, flexible batteries power transdermal medical patches for biometric sensing or intelligent drug-delivery systems. A wrinkle reducing patch uses an ultrathin, flexible battery to push dermatological agents into the user's skin more effectively than lotions or cream. [940]

7.3.10.3. Supercapacitors

Supercapacitors store energy by both ion adsorption (in electrochemical double layer capacitors (EDLC)) and fast surface redox reactions (in pseudo-capacitors). [941] Their recently enjoyed prominence as unique power devices is a natural extension of robust advances in the formation of ultra-thin conductive and insulating films developed for flexible battery technologies categorically, and novel atomic-thick films of graphene and nano-membranes specifically. When such ultra-thin films are overlaid or assembled with almost atomic precision, the result is the formation of large surfaces by rolling/folding of conventional double-layer charges and very large flexible capacitances. Today, it is possible to build supercapacitors that can pack a total of ~200 F/g specific capacitance per unit weight. [942-944] The figures are likely to climb higher as graphene technology improves contact resistance and nano-membrane spacers can be formed with greater accuracy and quality.

Both electrochemical double-layers and ultra-fast redox reactions can be formed with higher performance when the area increases and the separation distances decrease, which are

advantages naturally found in printed and flexible technologies. What makes supercapacitors especially important for FHE systems is their unique ability to operate in burst mode to provide high density of power for short durations. This cannot be delivered by standard batteries that contain larger energy storage capacity and cannot put that into action quickly in a safe manner, as indicated in Figure 99.

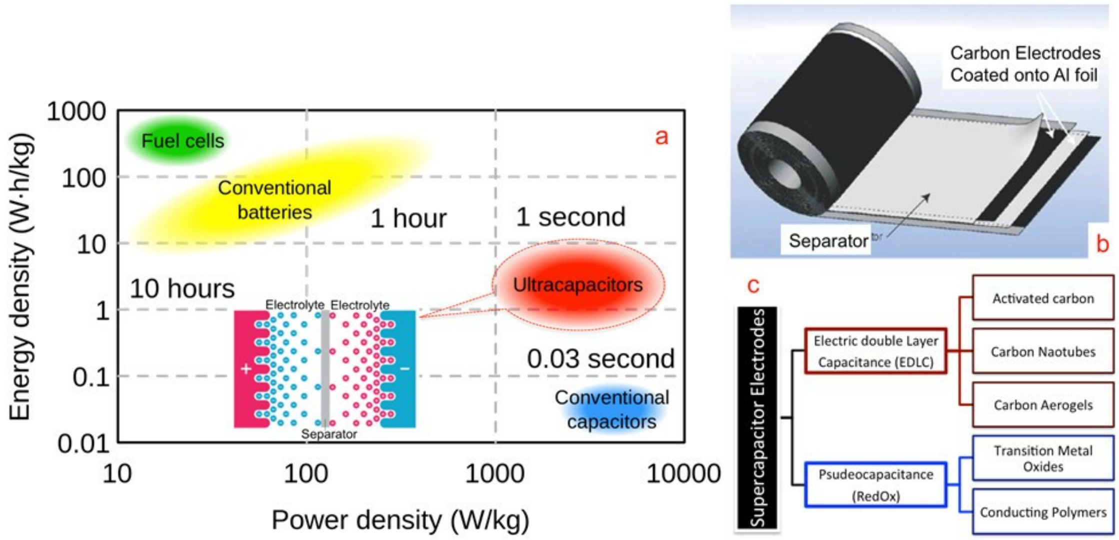


Figure 99. Demonstration of Performance and Structure of Supercapacitors [945]

Given the common technological basis, FHE systems naturally associate with supercapacitors, reducing battery size and weight in the process. This is true in FHE systems that must turn on/off between low and high-powered states, for example to transmit a burst of data at high rate, or FHE systems that may have to drive other electrical systems.

It appears that carbon electrodes printed on paper in the form of CNT or graphene are an especially interesting medium for supercapacitor integration. Aside from being extremely low cost and ultra-light, carbon printed supercapacitors also pack some of the best recorded performance figures. Figure 100 illustrates one such example that is stretchable by 200% in area for more than 1000 cycles and has extremely large (196F/g) capacitance. Graphene-enriched paper is mounted onto a pre-stretched elastomer to provide the stretching capability. It is helpful to point out that the capacitors in this example take about 100 seconds to discharge at a current density of 1A/g, which can indicate the significant potential of this technology.

Supercapacitors are just another tool that give FHE systems additional means to deal with the limited power problem, especially in systems where solar cells and energy harvesters exist alongside the battery pack to keep the system running longer. In this case, supercapacitors can even out fluctuations, provide much needed boosting power, and reduce load on the battery performance which results in longer battery life.

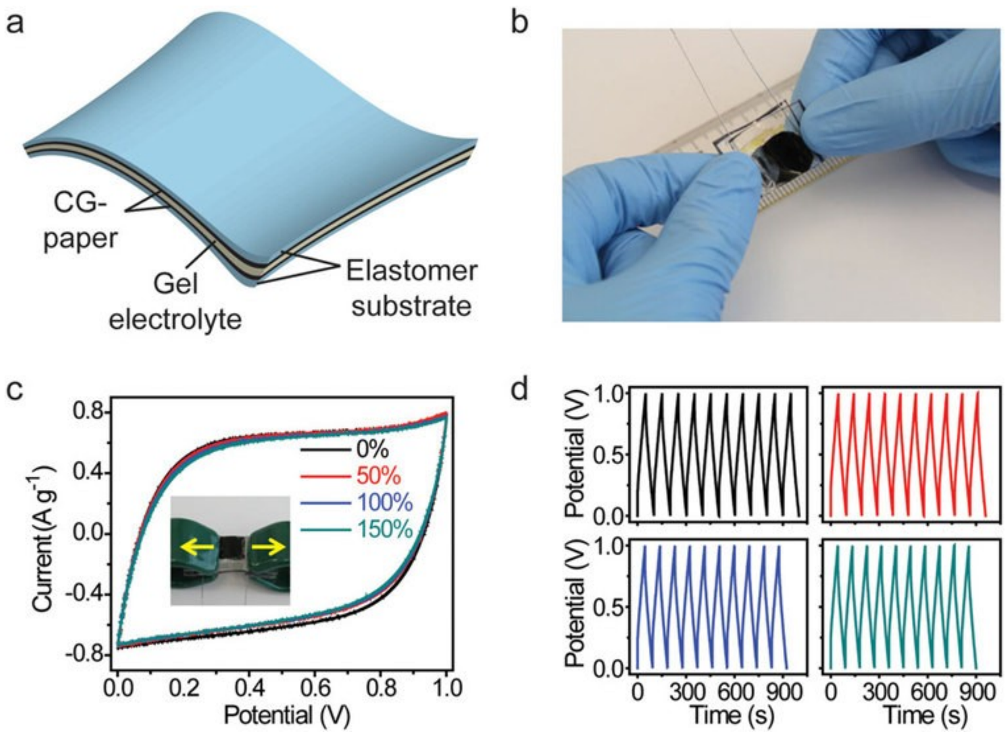


Figure 100. Graphene-Saturated Cellulose Paper-based Supercapacitor [944]

7.3.10.4. Flexible Photovoltaics (PV)

Along with other flexible devices, the development of organic solar cells has accelerated in the last two decades and led to formation of a large number of spin-off companies that are promoting products based on various flexible photovoltaic (PV) cells. These devices are not superior in performance to the conventional, solid inorganic versions based primarily on amorphous or crystalline silicon layers found in consumer products. However, the possibility of building extremely low-cost, flexible, semi-transparent photovoltaic generators that can be put inconspicuously on large surfaces like walls and windows is very attractive to broaden the use of PVs in a world challenged by access to affordable clean energy sources. Very similar to the case of battery technology, research and development work in flexible solar cells is already strong due to their huge market implications. Although their performance (~13% max. efficiency) and cost numbers are not yet sufficient for most critical applications, flexible solar cells can be still used in FHE to back up battery or supercapacitor packs. In unmanned aerospace applications where large surfaces and high-levels of solar exposure are available, they can be used as the primary power generator.

Three major classes of flexible PV devices exist, and they are categorized below:

- Inorganic semiconductors (amorphous silicon, CdS, CdTe, GaAs, etc.)
- Organic, small molecule, and polymer semiconductors
- Hybrid cells (a mixture of organic and inorganic semiconductors)

In the following paragraphs, these subclasses of flexible PVs, their applications, and their short term market potential are discussed.

Inorganic Semiconductor based PV: Conventional inorganic semiconductors are highly efficient solar cells which absorb light over a wide range of wavelengths and have high carrier mobility. Inorganic based PV is the most mature branch of PV materials with flexible capabilities. Normally, conventional manufacturing and processing of inorganic semiconductor type PV cells requires vacuum methods typical to semiconductor industrial process leading to high manufacturing costs. A number of companies are pursuing techniques to manufacture ultra-thin film inorganic PV cells in non-vacuum processes. [946] Currently, there are commercial producers of flexible, inorganic PV cells based on several material systems, primarily amorphous (a-Si), Cd Te, Copper indium gallium diselenide (CIGS), GaAs and related III-IV materials. Single junction and multi-junction flexible PV cells are available, with cost and performance being highly dependent on the material system chosen.

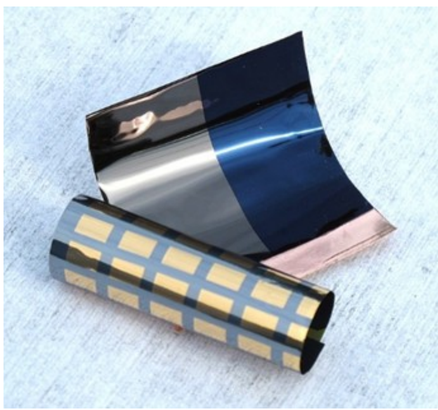
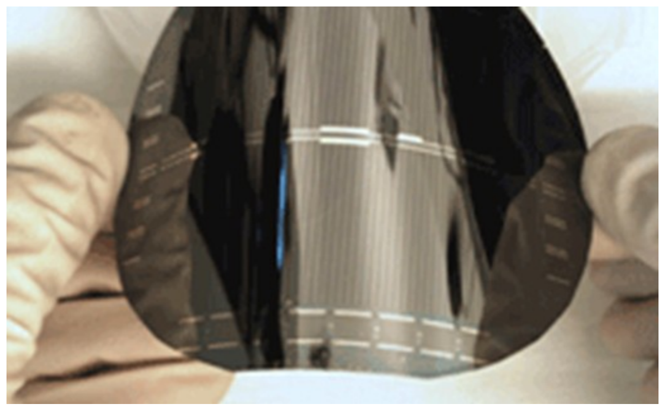
(a)  **(b)** 

Figure 101. (a) CdTe Based PV Cell & (b) Flexible Multi-junction GaAs PV Cell [947]

Production of a-Si cells generally requires vacuum processing techniques such as Chemical Vapor Deposition (CVD) and sputtering at temperatures up to 200°C, which allows for some plastic substrates to be used. Also a-Si solar cells can be made flexible by utilizing plastic or metal substrates and gain a competitive advantage over traditional crystalline silicon cells because of their thin film nature, which can be as much as 100 times thinner than current crystalline silicon cells (c-Si). Maximum module DC efficiency of a-Si PV cells is approximately 10%, significantly behind c-Si (17-21%). [946]

CdTe based PV have seen the most significant market growth in the thin film sector in the last decade. Empa, an interdisciplinary research institute in Switzerland, has achieved 13.8% efficiency for CdTe based cells on Kapton film superstrates, as shown in Figure 101 (a). [948] Production methods are similar to that for a-Si cells, with many companies using proprietary equipment based on standard processes. [843] Toxicity has historically been a concern due to the carcinogenicity of cadmium, but there is evidence that CdTe is not as toxic as elemental Cd. [949]

Copper indium gallium diselenide (CIGS) is another inorganic material system used in flexible PV cells. CIGS technology has received significant interest, but production is not as high as with other thin film materials, all of which considerably lag behind conventional c-Si, which accounted for approximately 85% of the PV market in 2011. [950] CIGS modules have typical efficiencies up to 15%, and the low cost of production make it an attractive alternative to c-Si

technologies. Production of CIGS PV is predominately coevaporation techniques under vacuum, however recent advances have produced CIGS thin films using electrospray deposition, which has the potential to be integrated into mass production processes like R2R. [951, 952]

The highest efficiency, and therefore most costly, commercially available flexible PV cells are multi-junction cells based on gallium arsenide (GaAs). Single junction cells made from GaAs are also available, and in a flexible form factor. Efficiencies of 28.8% and 31.1% for single and dual junction production cells have been noted by NREL [953] with triple junction cells capable of efficiencies as high as 38.8%. Module efficiencies for flexible GaAs cells are as high as 24.1%. [954] Historically, multi-junction cells have been used primarily for space applications and have had extremely high costs, mostly associated with material costs, and expensive processing methods, such as Metal Organic Chemical Vapor Deposition (MOCVD). Several manufacturers are now using proprietary processes based on MOCVD and similar vacuum techniques and have scaled production resulting in lower overall costs. An example is provided in Figure 101 (b).

Market share of thin film PV has declined compared to conventional rigid silicon technology in recent years, mainly due to the falling cost of silicon. Flexible inorganic based PV is expected to remain stable at approximately 9% of market share of total PV, with cadmium telluride (CdTe) and copper indium gallium selenide (CGIS) expected to be growth sectors through 2019. [955] This market share is not indicative of flexible PV, and includes all rigid, thin film technologies.

The current state of the art for most classes of inorganic PV cells is nearing theoretical maximums for efficiency and performance. Therefore, the remaining challenges for this class of PV cells are in manufacturing and scaling production, and in lowering material costs rather than materials research advances. Replacing vacuum and high temperature (>150°C) processing are critical to creating industrial scale, R2R processing for large area flexible PV. CIGS based systems have shown promise in solution based processing for cost effective manufacturing.

In addition to manufacturing challenges, inorganic flexible PV need to be reliable for an operating life approaching 30 years in order to be cost effective. CdTe and a-Si cells in particular degrade significantly under normal operating conditions. However, if PV recycling can prove cost effective, lifetime performance is less of a concern.

Organic based PV: Organic semiconductors have received considerable interest in the last decade despite significantly lower efficiency compared to inorganic PV cells. The work first showing potential for organic PV was first published in 1986. [956] Large area and low cost manufacturing, a wide range of materials, and property tailoring create significant advantages for organic PV cells. Organic based solar cells use a wide array of conductive polymers and other small organic molecules in addition to low cost plastic substrates to create a cost-effective PV solution. High optical absorption coefficients combined with tunable energy gaps in active polymeric materials are advantages of organic PV cells, but low efficiency and stability over time are disadvantages. [957] Single junction, bilayer, discrete, bulk and graded heterojunction type cells have all been produced, and research in all types of cells continues, with a focus on multi-junction type cells. [958] An emphasis on renewable, low environmental impact materials has driven research into other areas as well, including dye-sensitized and nanomaterial based hybrid PV systems. [843]

Efficiencies of OPV cells are much lower than inorganic based PV cells, in the range of 3-5% for most devices and about 10-11% for world record research cells. [953] The greatest opportunity for advancement in OPV lies in material research for improving efficiency. Since materials used in OPV do not include silicon, there is little price fluctuation or competition with the semiconductor market. However, the recent glut of polysilicon materials has resulted in a resurgence of traditional PV manufacturing, leading to the collapse of several OPV research companies. Raw materials required for organic PV materials are abundant, but the quality required for PV systems is generally absent, creating another obstacle for OPV.

Companies such as General Electric, Konarka, Nanosys, Nanosolar, Plextronics, Solaronix, Shell, Sharp, Sony, CDT, Toshiba, Global Photonic Energy, and Quantum Solar are performing benchtop research and development as well as pilot scale-up programs for organic based PV. [843] Konarka and Plextronics were both producing thin, flexible organic PV devices and raw materials before going bankrupt (June 2012 and January 2014 respectively). Plextronics was acquired by Solvay (Brussels, Belgium) to increase OLED development within Asia in 2014. [959] Recently, researchers at Technical University of Denmark have demonstrated large area R2R manufacturing of tandem (bilayer) flexible organic PV cells under ambient atmosphere conditions. [960]

Hybrid based PV: A combination of both organic and inorganic materials, hybrid type PV cells combine advantages of flexible inorganic and organic PV – low cost materials, ease and scalability of manufacturing, and high theoretical efficiencies. Hybrid PV cells incorporate semiconducting nanomaterials in an organic matrix, yielded bulk heterojunction PV cells with good electron transport and light absorption. [961, 962] For instance, altering the size and shape of the semiconductor nanomaterial has resulted in optical band gap tuning for CdSe nanorod polymer PV cells. [963] Hybrid PV cell processing can be done in solution or vapor assisted techniques, both of which are significantly cheaper than traditional PV and inorganic processing methods. Other hybrid PV cells include polymer nanocomposite (fullerenes, CNTs, CdSe nanoparticles, etc.), dye sensitized, and perovskite materials among others.

Perovskite cells are named so because they include a material with a chemical formula ABX3. The most frequently used materials in perovskite PV research is methylammonium lead trihalides (CH3NH3PbX3 where X is a halogen ion). As with OPV, hybrid PV technology maturation will depend on materials research and large scale manufacturing integration. There are some toxicity concerns for lead based perovskite PV. Perovskite type hybrid PV cells have seen dramatic increases in efficiencies since 2009, from ~3.0% to an NREL certified 20.1%. [953] This rapid improvement has lead perovskite based PV cells to be a breakthrough technology of 2013 in leading journals. [964, 965] Hybrid PV cells are currently limited to research rather than production, but some startup companies hope to bring perovskite based hybrid PV to market in 2017. [966] Hybrid PV cells must overcome challenges such as lifetime performance and degradation before large-scale manufacturing occurs.

Dye sensitized cells generally use a wide band-gap TiO2 inorganic semiconductor with an organic based dye, which can be printed over a large area. However, their architectures are significantly more complex than traditional PV cells and the challenge of packaging gels or liquids in a large scale functional device has slowed commercial interest. Efficiencies for dye

sensitized cells peaks around 11.9%, and much lower for other hybrid cells, typically less than 5%.

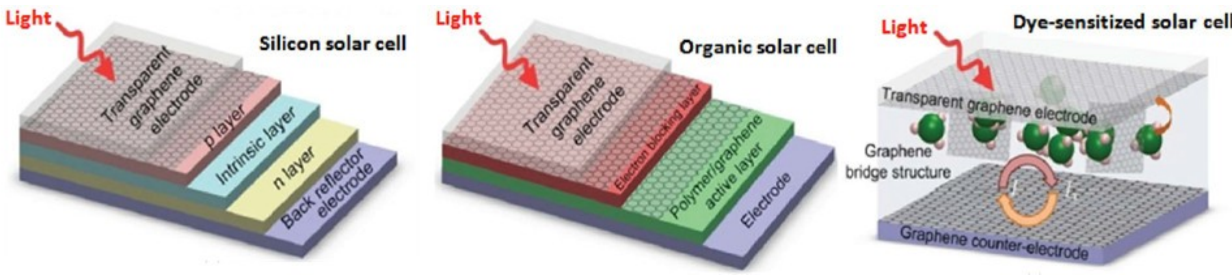


Figure 102. Flexible Organic Photovoltaic Devices [791]

As mentioned, some of the main classes of flexible solar devices that can be applied to FHE systems include: (1) dye-sensitized metal oxide cells; (2) organic polymer-based cells; (3) perovskite solar cells; and (4) nanomaterial-based (graphene, CNT, nanowires, quantum dots, etc.) novel devices. There are also composite devices that attempt to combine several such devices in tandem and ternary arrangements. Figure 102 shows the general structure of some of these devices. Some of the latest efficiency results of these alternative approaches are provided in the mega-efficiency (power conversion efficiency – PCE) table provided by NREL in Figure 103, which shows the performance of conventional PV devices as well as other experimental efforts based on III-V semiconductors and organic materials.

Although flexible/organic PV and other emerging PV technologies struggle in performance, peaking at ~13% (see red lines in chart of Figure 103), their rapid progress in output performance is not matched by any other technology. At this rate of improvement, and by combination with other techniques or in tandem cell arrangements, flexible PVs can become serious contenders for applications that can accommodate large areas and have ultra-low power or cost requirements. This is good news for FHE systems for several reasons: low-cost, ultra-light, and directly printable power sources can be extremely helpful for many defense-related avionics, wearable communications, and monitoring applications. For civilian modules, many autonomous and low cost systems can greatly help in forest/bush fire control, infectious disease control, traffic monitoring systems, first-aid responses, etc.

As shown in Figure 103, organic/flexible PVs is a rapidly growing and vibrant research domain with multiple complementary approaches. Although a complete review of these many device approaches is not possible in this brief overview, several prime examples that can impact FHE design and development are shown in Figure 104 and Figure 107. Solution-based printed approaches are especially suitable for low-cost flexible transparent top electrodes. The added benefit in this case is the inclusion of nanomaterials that can reduce reflection and loss at the electrical contacts, finely tune absorption spectra, increase absorption, and be coupled with inorganic solar cells or other energy harvesting devices as described in Section 7.3.9.1.

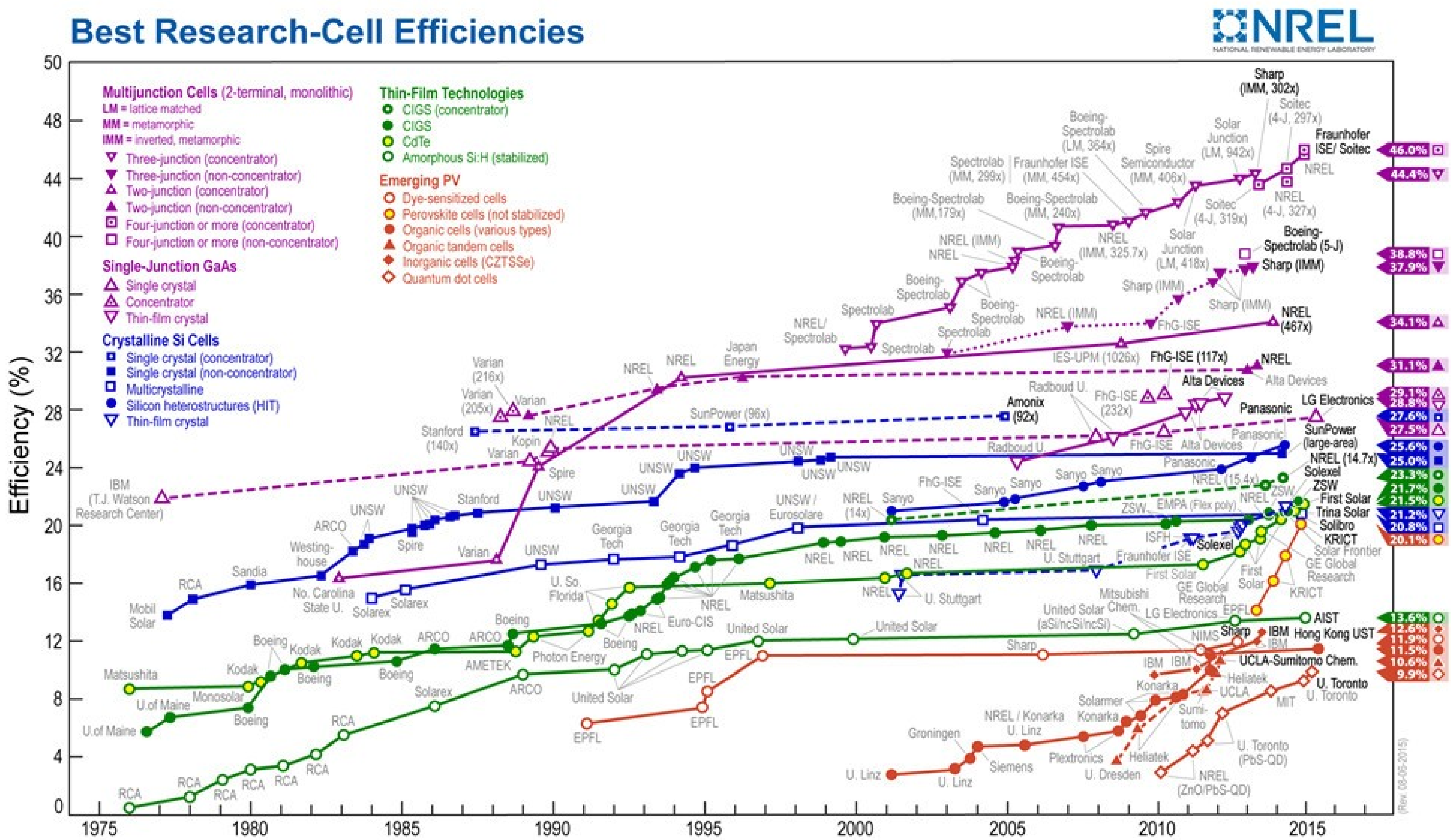


Figure 103. Efficiency Meta-chart by DOE'S NREL [967] to Compare Existing PV Technologies (Including Organics)

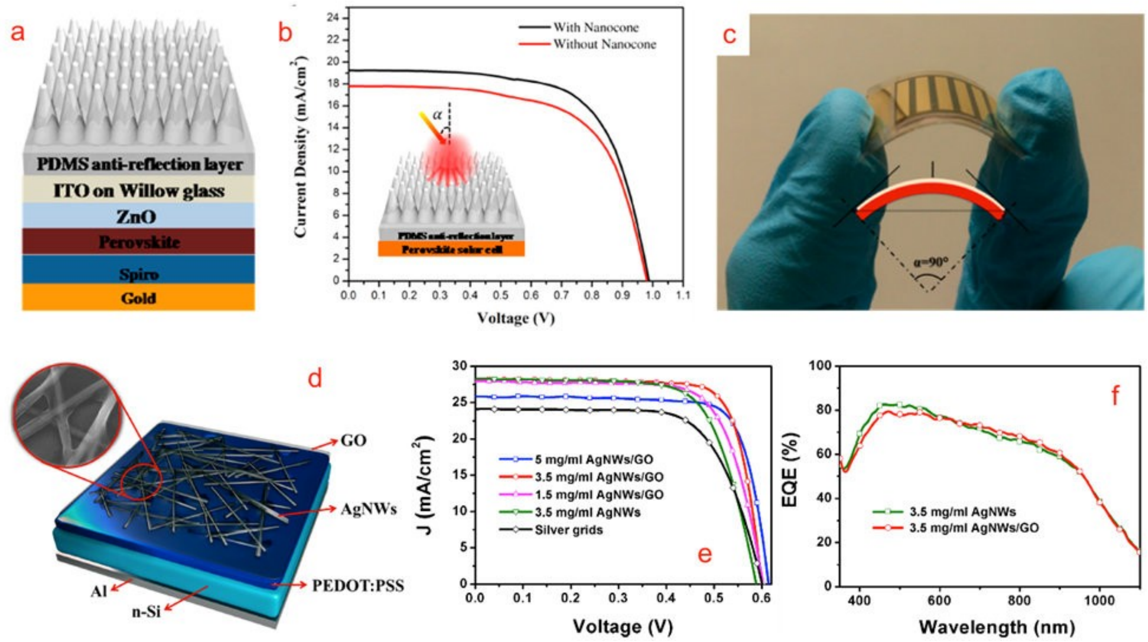


Figure 104. OPV Technology: (a-c) Record-Breaking Perovskite/ZnO Cells [968]; (e-f) Inorg. (nSi)–Org. (PEDOT:PSS) Hybrid Cells with Nanowire Top Contact [969]

Application Examples/Opportunities for FHE PV – Applications of flexible PV cells are obviously related to power generation and delivery. Flexible PV has significant advantages over traditional crystalline PV cells in size, weight, durability, and portability, making it useful for powering anything that can be carried, worn, or moved. Current practical applications of flexible PV are a significant majority of inorganic based PV system due to their higher efficiencies. A number of flexible modules are available for battery charging for numerous civilian and military devices, including but not limited to GPS, radios and communication equipment, computers, night vision googles, lighting systems, and small vehicles. Marines and other US military branches have experimented with backpack mounted flexible PV modules for a number of battery charging applications (Figure 105). [970] Tents (Figure 106) integrated with flexible PV have been utilized in military capacities since 2010. [971] Thin film PV technology is being investigated for military applications because it has the potential to offer low to no heat signature. [972]

Curved structures such as cars, planes and other vehicles are ideally suited for flexible PV integration. Alta Devices and MicroLink Devices have both produced thin, flexible inorganic PV modules for UAVs [973] shown below in Figure 106. These companies technologies are in GaAs based PV.

Figure 105. Backpack Mounted PV Module [970]

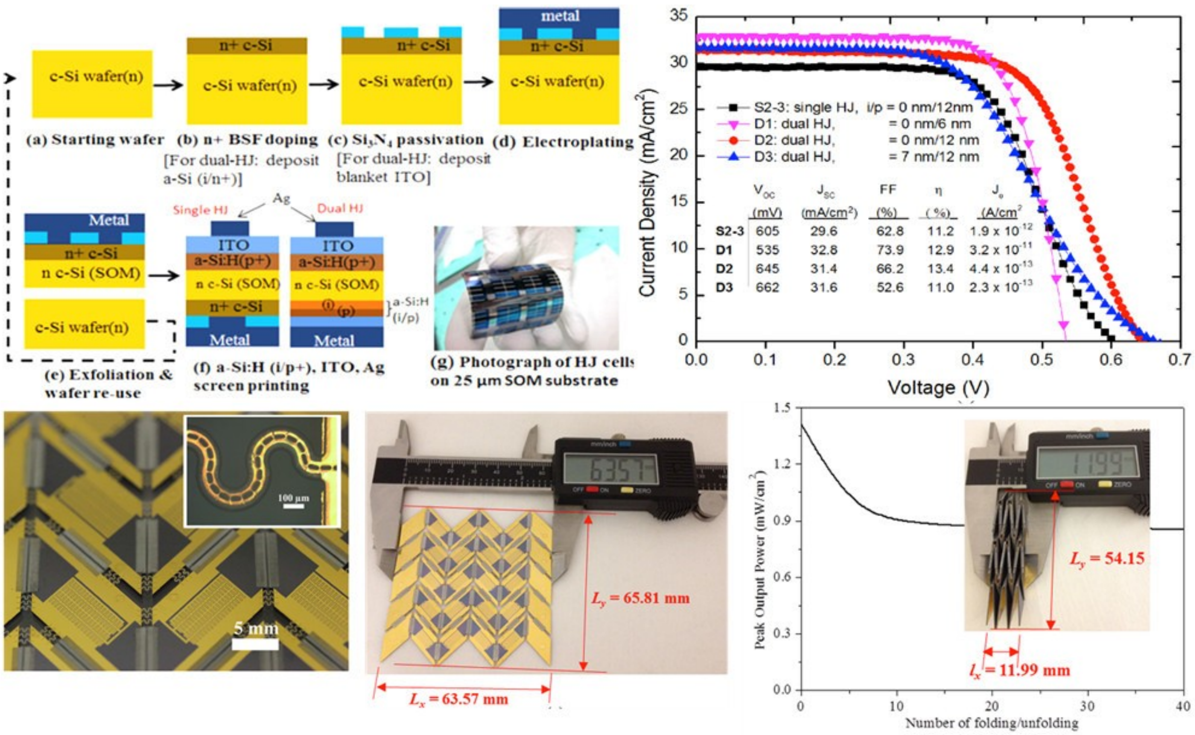
Figure 106. Unique Applications for PVs: (left) Tent with Flexible PV Panels & (right) UAV with Supplemental PV Power [973]

Applications for OPV cells are currently limited to niche applications. The opportunity for low-margin consumer electronics, such as calculators, toys, and musical greeting cards will exist in the next 3-5 years. [843] Large area OPV for applications currently occupied by inorganic PV systems must overcome efficiency and stability issues before system integration is realized. Improvement in energy storage and conversion (batteries, capacitors, etc.) could help implement OPV sooner. Hybrid cells and OPV cells can also be made transparent, which could lead to additional inclusion in BIPV applications such as window glazing or transparent coatings for building exteriors.

FHE systems have a very pragmatic and 'flexible' view of integration: if FHE cannot beat a technology by direct printed techniques, then it can welcome it as an add-on device, as in the case of CMOS ICs. High performance solar cells are another potential example for this pragmatic approach. In applications where PVs are indispensable or the only source of energy, and printed/organic solar cells are inadequate in performance, FHE may integrate conventional and expensive record-breaking solar cell technologies (see upper end of Figure 103) such as III-V tandem cells or quantum dots that cannot be made onto large surfaces for commercial purposes. To do so, FHE may use approaches similar to those used for transfer-printed CMOS or stamping techniques such as those developed by the Rogers group at UIUC. In small areas, compact solar cells can be integrated on pre-stretched elastomer surfaces to gain stretchability that can be used to actively change 'cell' density as the solar light intensity varies during the day (i.e. cooling) or for deployment on curved surfaces.

7.4 Important Forces Affecting FHE Development

Before exploring the future directions and applications for FHE systems, it will be helpful to summarize overall FHE development trends identified so far and reconsider important forces that are expected to shape the technology and the marketplace. By keeping these factors in mind, a more accurate and balanced evaluation of FHE's future potential may be established. Such evaluation is attempted in the following sections.



	V_{oc} (mV)	J_{sc} (mA/cm²)	FF (%)	η (%)	J_o (A/cm²)
S2-3	605	29.6	62.8	11.2	1.9×10^{-12}
D1	535	32.8	73.9	12.9	3.2×10^{-11}
D2	645	31.4	66.2	13.4	4.4×10^{-13}
D3	662	31.6	52.6	11.0	2.3×10^{-13}

Figure 107. Thinned Si Solar Cells [974] (top row) & Micro-Machined Foldable Si PV Array [975]

Pragmatic Integration – The first and most important characteristic of FHE development is the fact it is a pragmatically driven effort, motivated solely by the need to optimize the combination of options offered by two worlds: flexible technologies and conventionally integrated systems. In this pragmatic effort, FHE aims to bring together low-cost, ultra-light, and efficient solutions on flexible substrates with conventional technologies if they can be integrated with novel form factors (size, packaging, and operation conditions). The line that separates FHE from so-called printed electronics is the FHE industry's willingness to integrate ready and mature solutions in contexts where novel printed devices cannot provide the necessary size, performance, or power requirements. In other words, a specific manufacturing or device technology does not drive FHE development per se, as is the case for silicon CMOS technology. Instead, FHE is based on a strong will for mixing and matching adequate solutions as long as they can co-exist on the same 'flexible' substrate. If anything, it may be reasonable to argue that FHE is a 'flexible substrate' driven composite technology.

Fragmented Technology – The second unique characteristic of FHE development is its composite nature that is challenging for designers as well as manufacturers. For FHE optimization, multi-talented design teams with the ability to handle multi-scale problems are

necessary. This includes awareness to work with many novel materials (organic as well as inorganic), multiple unconventional integration techniques (printed versus packaged), complex signal domains (mixed-signal analog and digital systems, power, RF, optical and mechanical), and unfamiliar applications. While the toolbox of FHE engineering is very rich and 'flexible', which may be viewed as an advantage, it also presents challenges for all involved, including those who must develop manufacturing tools, designers that must choose from a multitude of sensors and devices, and users that must utilize this novel technology in a productive and safe manner. This composite nature is also reflected in civilian and defense uses of FHE systems: even for products or designs that are most clearly of interest to the defense domain, FHE can easily find broad applicability to civilian contexts. This is because FHE systems by default may lead to more portability and lower SWaP footprint, which are equally important for mainstream products today. In return, consumer applications may provide the production volumes that the defense market lacks.

Market and Applications – The final distinguishing aspect of FHE development is its broadly recognized, yet not clearly defined, application potential that tends to expect a '*killer product*' that will distinctly identify the advantages of the technology in a specific context and provide higher financial incentives for investment, manufacturing tool development, and design focus. Much like in the case for MEMS in the early 1990's, most stakeholders agree regarding FHE's implications for electronics systems design and manufacturing. However, it is not yet sufficiently clear how and in what unique product this impact will materialize first. In fact, the resemblance between FHE systems and MEMS development in the early 1990's is quite interesting and can provide assistance in analyzing future trends. For instance, MEMS' '*killer application*' was a digital micromirror device (DMD) developed by Texas Instruments that surpassed all existing projection systems in size and performance, and the surface micro-machined accelerometers that were key for airbag deployment and pacemakers. It took, however, 10 years to develop, with a hefty price tag, and the whole field of MEMS needing to wait until the late 1990's before becoming a financial reality.

Keeping these general observations in mind, the following sections describe important forces that are expected to shape capabilities and opportunities of FHE systems, to answer this very question of the killer or flagship application. No particular order of preference is implied by the order of presentation of these shaping forces.

7.5 FHE Market Projections

Several professional consulting companies (YOLE, Parc/Xerox), industry associations (iNEMI, SGIA, IDTechEx, FlexTech Alliance), and researchers have commentary on the FHE market and its future potential. Invariably, these reports are driven by different needs and agendas, and each report emphasizes certain critical features, most focusing on printed technologies rather than FHE. Their difference is especially amplified in the future market potential and application focus that they consider important, as shown in Figure 108, Figure 109, and Figure 110. For instance, IDTechEx predicts a $70B market by 2024 (Figure 108), whereas YOLE projects a mere $1B by year 2020 for the combination of flexible and printed electronics (Figure 109). While some of the difference is due to the definition of market segments, there is also a varying level of realism injected into the projections. For instance, IDTechEX includes all printed and flexible devices, including those that may not necessarily fit within the context of FHE applications such as stand-

alone organic displays (the largest segment by far), solar cells, batteries, or sensors. Regardless of the numerical and semantic differences, what is clear is that flexible and printed technologies, either alone or found in the FHE context, are going to expand rapidly. Without identifying applications, it is difficult to speculate on the FHE systems' share in these projections. However, it is fair to indicate that with the IC adaptation and increasing maturity of FHE systems, these figures can go up significantly.

A significant amount of speculation exists in the estimates and studies mentioned above, as to how the FHE market will evolve in the next 25 years. Countless reports and studies have been published in an attempt to document this type of market and forecasting information. For example, the Large Area, Flexible Electronics Chapter of the International Electronics Manufacturing Initiative (iNEMI) 2015 Roadmap identified medical, automotive, and wearable/consumer applications as the most promising near-term commercialization opportunities for flexible electronics, and within these three application areas, the roadmap mentions that lighting/displays, sensors, and energy devices will be driving most of the development for the near future.

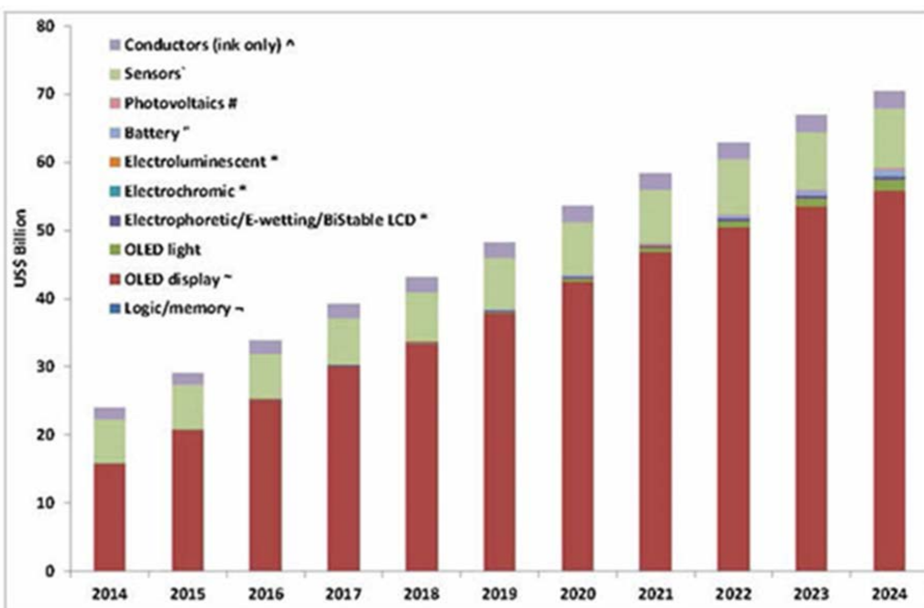


Figure 108. IDTechEx: Market Potential for Flexible & Printed Technologies [976]

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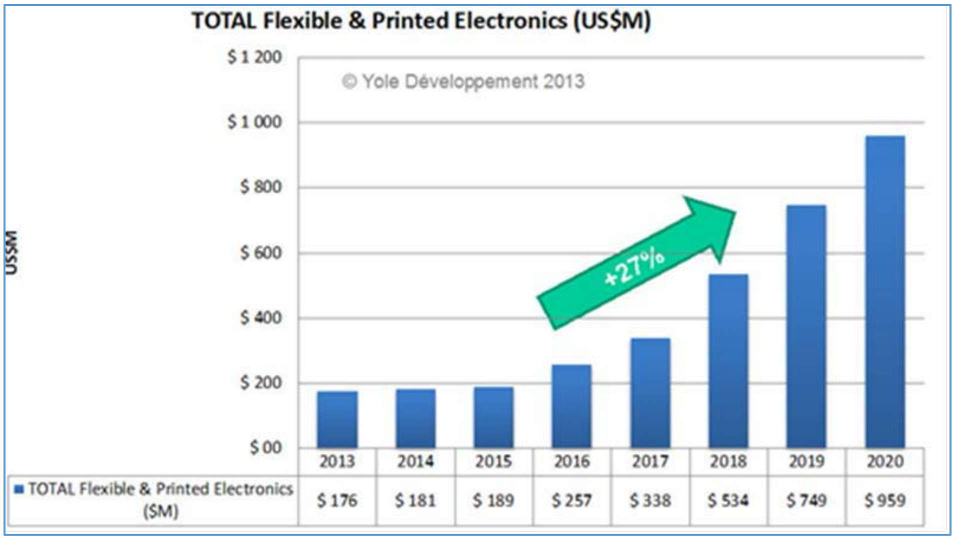

Figure 109. Yole Development Surveys: Market Potential for Flexible & Printed Technologies [87]

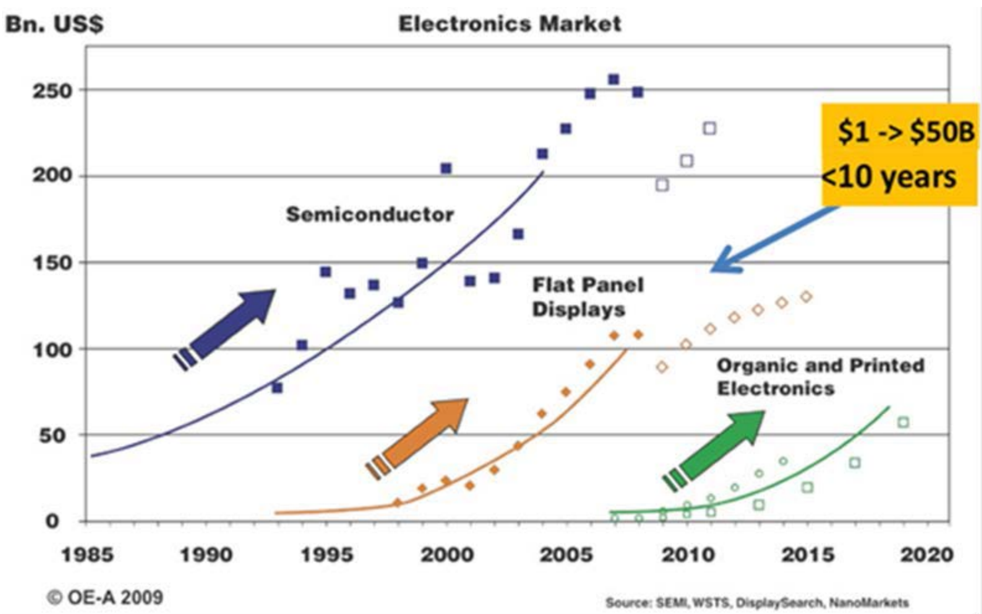

Figure 110. Growth of Various Areas of Electronics Market [797]

7.6 Problems & Opportunities in FHE Development

In accordance with the forces in action and device toolset introduced earlier, in this section we will evaluate the potential problems and indicate opportunities for FHE technologies before presenting projections for the next 25 years. Like in all technological developments, with each challenge can come unique opportunities that can lead to surprising outcomes that often go beyond the original objectives. Thus, additional thrust for FHE development may as well come from one of the following challenges.

7.6.1 Limited Heat Conductivity & Ultrathin Metallic Foils

Perhaps the biggest problem for flexible substrate technologies, before cost and mechanical limitations, is their limited heat conductivity that can present a stumbling block for FHE technologies. As indicated earlier, pragmatic definitions assume that high performance surface mounted, thinned, or transfer printed CMOS chips will be integrated onto true FHE solutions. This makes power dissipation a serious concern and, given the heat sensitivity of the substrates, it is a challenge that affects in two ways. Power dissipation can increase overall system operating temperatures, which in itself is detrimental. Moreover, heat trapped in the substrate can also become a serious liability for the plastic/paper/textile substrate itself, especially for long-term electrical and mechanical reliability of the system. Given that most FHE systems may be placed in harsh environments or users themselves (i.e., for wearables), this makes the heat problem triply important, which implies that it must be resolved before a significant jump in FHE development and widespread use can become a reality.

TECHNOLOGY GAP: FHE SUBSTRATE ENGINEERING

Currently most FHE development work takes place on a simplistic, single-material, and layer substrates that are optimized predominantly for one functionality (weight, flexibility, transparency, and so on). Substrates used for FHE system development should become more sophisticated in terms of function and structure with parts focusing on different outcomes or functionalities.

POTENTIAL SOLUTION

Borrowing ideas from complex packaging materials developed and low-cost R2R manufacturing approaches, affordable novel multi-functional substrates (paper substrates on metal foil meshes, textile on stretchable perforated plastic layers, etc.) can be produced. Such substrates can mitigate some of the noise, reliability, and heat conductivity concerns without sacrificing form factor and flexibility.

As a new substrate alternative, *metallic foils* can present a possible solution to the heat dissipation problem as well as a unique alternative to the durability problem of the flexible substrates in harsh environments. Ultrathin (1-10µm) metallic foils of copper, steel, and nickel may be used in many FHE applications as substrates with excellent thermal conductivity as well as better durability. Such thin foils have sufficient ductility and elasticity that can rival plastic substrates and surpass paper films. Since they can remove a lot more heat at a faster rate, while also serving as a better shield for RF and ionizing radiation, metal foils may present excellent options in the short to medium term for the power problem, while also adding a new twist to the substrate options. Metallic foils should not be considered as a replacement to the existing substrates, but rather as an additional layer in laminated substrates. For instance, ultra-thin copper layers can be deposited or bonded to the back of polyimide (Kapton®) substrates used for assembly of the FHE system. To reduce weight and maintain flexibility, the copper layer can be also reduced to a mesh. Having a copper backplane can also have benefits beyond heat removal for a variety of other devices (besides FHE devices) including but not limited to solar devices, reflective displays, RF sensors, patch antenna designs, and co-planar waveguide structures. Similarly, textile and paper substrates can have embedded metallic threads or foils that can expand their potential for cooling, while also improving additional electrical and mechanical

characteristics. Thus, metallic foils and metal/substrate composite structures should be considered carefully for the next phase of flexible substrate development.

7.6.2 Limited Power & Flexible Energy Ecosystem

It is generally accepted that FHE systems' biggest impact, at least in the short term, could be in portable and distributed information systems, ultra-light and autonomous vehicles such as drones, structural and biomedical health monitoring systems, and low-cost transportation systems, i.e., applications that value reduction in SWaP footprint. For many of such systems, access to power is either intermittent or limited, which would require FHE solutions to consume ultra-low power levels on one end and to harvest energy from ambient sources into efficient and compact battery packs on the other. Thus the *limited power* problem has implications at two levels of design: *operational limitations* and *complexity of power infrastructure*. Assuming that there is sufficient cooling, the former can determine the upper limits on the number of adapted (thinned or transfer-printed) ICs in the system, size of the displays, or range of communication or travel, while the latter severely affects the system SWaP since large areas are necessary for either harvesting or storing considerable amounts of energy.

Operational limitations and the number of ICs adapted are decided based on the system functionality and cannot be arbitrarily scaled as needed. This implies that the complexity of the power infrastructure is the key parameter in determining the application domains and types of solutions that FHE can propose. Since current solar devices are unlikely to be sufficient for demanding applications, use of other harvesting devices (vibration, heat, stretching, RF, and so on), supercapacitors and efficient battery systems, or even fuel cells may be necessary to extend energy sources and tackle peak power requirements. Therefore, in FHE applications where power levels and autonomy are indispensable requirements, a highly complex and robust power infrastructure with access to multiple energy harvesting tools is the key to future developments. This is to say that the ability to create and manage a complex power-engineering ecosystem on flexible substrates may as well decide the fate of future FHE systems. Creative solutions in the energy harvesting and power engineering front is a requirement if FHE technology is to reach its intended impact and become a technology that serves a role beyond several specific applications in the defense domain or as means to create more intelligent digital 'toys' or low-profile sensor interfaces for specialized sets of problems. Creation of a 'green energy ecosystem', both in terms of peak power and total energy capacity, would pay dividends well beyond simply powering FHE systems, by becoming a product on its own that empowers FHE development as a whole.

TECHNOLOGY GAP: INTEGRATED ORGANIC/INORGANIC POWER PACKS

Integrated power modules that combine essential elements of a power infrastructure (harvesters, PVs, generators, inverters, regulators, batteries, and supercapacitors) in a very efficient, compact, and scalable manner would ease not only FHE system development but can become a product on its own. Such combined modules on textiles can result in exciting FHE products including wearable electronics, biomedical and environmental monitoring systems, and UAVs that can remain airborne for extended periods.

POTENTIAL SOLUTION

To become serious alternatives for powering civil and military FHE systems and make an impact in conventional markets, a power ecosystem developed on flexible substrates must better align and standardize in terms of material sets and manufacturing tools. Where possible, integration of multiple devices on the same surface or layering of different solutions without sacrificing flexibility would be necessary.

Currently, the practical limit for energy harvesting, including organic solar technology, is around ~1mW/m2, depending on the application and size. In the medium term, with better performance and 3D integration it may be conceivable to reach ~10 mW/m2 level, at which point more FHE applications may become possible. However, when FHE systems can generate, store and deliver ≥ 100mW/m2 level power on flexible surfaces, the true potential of FHE systems can be unleashed in many autonomous and agile applications, both in defense and civilian domains. Therefore, in the short term, a practical target for the flexible energy ecosystem and complex power infrastructure for FHE systems is 10 mW/m2, which must be scaled to 100 mW/m2 in the medium to long term.

7.6.3 Limited Area & 3D Integration

The motivation for many FHE applications is to reduce SWaP requirements and gain flexibility in physical design. This implies in many cases that the final product is ultra-compact and light. However, for several devices such as solar cells, batteries, displays, and antennas, the overall area available would matter and improve the performance or functionality required. Hence, there is a degree of an inherent paradox in ultra-compact FHE products that may limit applications to those that can have access to large area for energy harvesting or efficient battery performance. To address this issue and increase room for additional sensors, circuitry, and power devices, it may be necessary to build multi-layered FHE systems that still retain sufficient levels of flexibility and agility. This will only be possible if each layer has sufficient flexibility to start with and folding or multi-layering of the overall system will not impact its intended operation by interference, blocking of signals, or increasing heat. Therefore, especially in the medium to long term, the ability to design and manufacture multilayered FHE systems may become a critical issue.

A similar but more complex 3D integration problem is already being tackled by the silicon CMOS technology. At the end of Moore's scaling, when further miniaturization is no longer practical and affordable, 3D integration is one of the very likely scenarios for the conventional silicon technology, as also indicated in Figure 111. It is a requirement, especially for system-on-chip (SoC) designs where an entire chip is integrated on a single piece of silicon. For SoCs, 3D

integration also makes economic sense, since the yield would be higher: a single defect that can occur during fabrication would not risk the functionality of the entire system. Also, components from various suppliers and technologies can be assembled into the final design, which provides additional ‘flexibility’ in economics as well as enhanced system functionality.

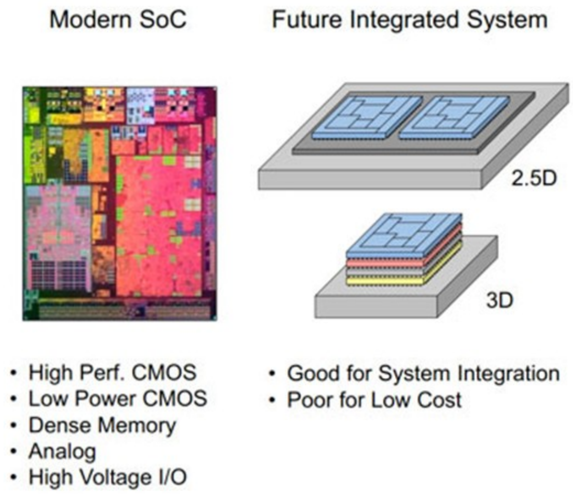

Figure 111. Vision of Impact of 3D IC Technology

Digital systems that require large amounts of on board/cache memory are also likely beneficiaries of 3D IC integration. So are mixed-signal systems that utilize separate processes for digital and analog subsystems and high frequency RFIC chips that must incorporate multiple inductors and antennas on chip. In fact, there are multiple 3D IC examples already [978] and the ITRS roadmap considers 2015 as the year of market entry for many 3D IC products. All the experience gained from 3D integration of CMOS ICs can have important ramifications on the development of future FHE systems. First, it may be possible to adapt the 3D ICs into FHE solutions, which would help the area limitations and provide additional functionalities for FHE-based products. This would generally help alleviate power and area limitations in FHE designs, yet may lead to further complications related to the heat removal problem if aggressively applied. Therefore, 3D IC integration of ultra-low power mixed-signal systems presents unique opportunities for FHE system development that need to be carefully examined.

Just as importantly, it must be pointed out that wafer thinning or transfer-printing technologies that are developed largely for adapting ICs on FHE systems are also applicable to 3D IC integration. Therefore, the two technologies have common manufacturing elements that can be mutually rewarding. Since market potential of 3D CMOS ICs is bigger and the need is more urgent, FHE systems may benefit indirectly from 3D IC manufacturing technologies that can lower cost for IC adaptation. In return, it is conceivable to expect that large passive device components such as inductors, super capacitors, and antennas that are perfected for FHE systems can be built by printed techniques and integrated into 3D IC fabrication sequences. In other words, the relationship between FHE systems and 3D integration is a one-way, but a symbiotic one. Both technologies have something to offer and take in 3D integration efforts. Given the implications of 3D IC integration also for packaging solutions, it is obvious that this symbiotic relationship can rapidly grow important for all sides concerned, much sooner than most expect.

Consequently, it is *necessary* to monitor how 3D IC technologies develop in the next couple of years to understand its impact on FHE systems.

7.6.4 Photonics Integration

Photonics and optoelectronic devices such as solar cells, photodiodes, LEDs, and displays are prominently used in FHE products and may be the key elements in some applications. However, photonics technology has much broader capabilities that can be applied to FHE systems. There is a notable absence of many advanced active and passive photonics devices (lasers, optical amplifiers, waveguides, resonators, and so on) that can be used for efficient high-speed data communication and sensors with ultra-high (down-to single molecule) sensitivity. [979] Figure 112 presents several such photonic devices from very recent publications. [942] Clearly, organic materials, printing techniques, and flexible surfaces should not be considered off-limits for photonics technology, which can have much more to contribute. It appears that the current unfortunate gap in flexible photonic research is likely to close in the next few years and FHE systems may expect many more devices to exploit from photonics technologies in the years to come.

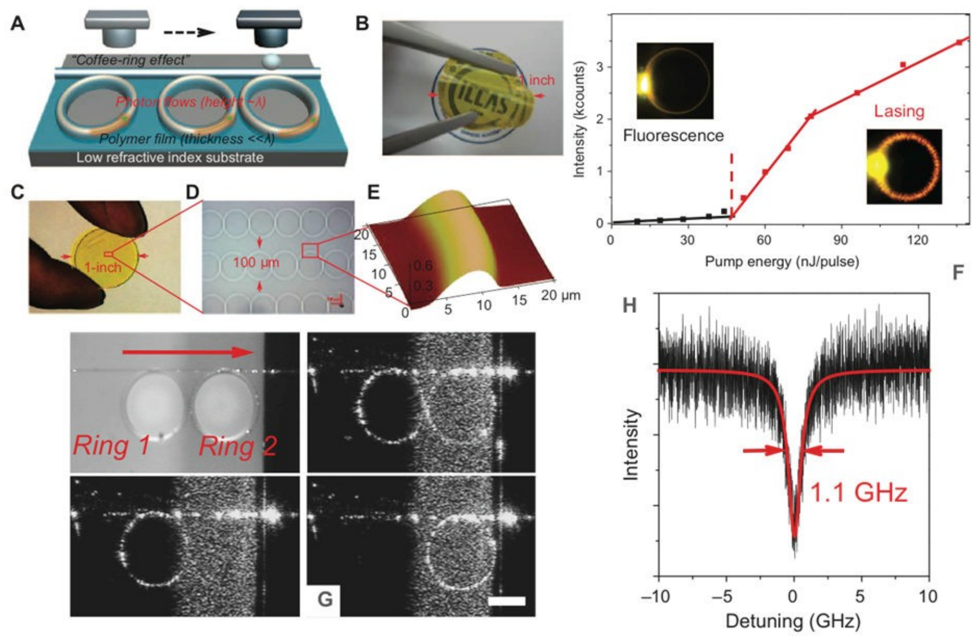

Figure 112. Examples of Organic Photonic Devices: (A-E) Ring Resonators (RR); (F) Optically Pumped Laser in RR; G) Coupled RR; H) Ultra-High Q-factor [942]

TECHNOLOGY GAP: PHOTONICS INTEGRATION IN FHE SYSTEMS

Photonics communication and sensing technologies are currently lagging behind organic displays, imaging, and PVs with respect to their use in FHE systems. Greater use of these technologies, especially in wearables, should produce exciting opportunities in sensing and ultra-low power and high-sensitivity solutions that may not be found in electro-mechanical signal domains.

POTENTIAL SOLUTION

Adaptation of fiber-based photonics technologies onto textile surfaces and into fabrics as well as development of fiber-mounted LEDs and solid-state lasers can greatly facilitate the use of proven photonic sensors and communication tools for FHE systems. Multi-mode plastic fibers and creative use of non-chromatic low-power photonic devices may be necessary to achieve flexible performance.

Research on optical communications on flexible substrates via printing techniques currently trails electrical devices in maturity and complexity. Instead, there is a disproportionate concentration of fiber-based photonic applications in wearable and textile-based flexible applications. However, this situation is likely to change rapidly thanks to demonstration of all-organic lasers, waveguides, optical amplifiers, and modulators such as those presented in Figure 112. This would mean that optical communication devices could also be built using solution-based printing techniques on flexible substrates, much like any other electrical component. However, optical communication and sensing often implies fast data rates that must be accompanied by ultra-fast electronics. Such high electrical carrier mobility is current evading printed electronics for the most part. Thanks to carbon-based electronics and novel nanomaterials, this can be circumvented by several approaches, and should not be considered an insurmountable barrier. Plasmonic effects in metallic nanoparticles, graphene-based THz devices, transfer-printed III-V ICs, as well as non-linear optical effects may provide alternative approaches to address the speed problem that will always challenge organic photonics. Even if ultra-fast electro-optic effects may not be available in the short term, certain photonic devices that offer record Q factors, energy efficient and interference-free communication, or unique sensing schemes can be still employed in FHE systems. This is especially true in textile systems that have already shown many examples of integrating optical fibers into fabrics for sensing and decorative purposes. Their flexibility and robust structure allows optical fibers to be seamlessly integrated into textiles and used for both structural and optical functions, paving the way for a variety of mature fiber-optic devices (lasers, amplifiers, and sensors) to be integrated into wearable applications and other FHE systems.

7.6.5 Flexible Packaging

Flexible packaging technologies is yet another strategic area that presents both problems and growth opportunities for FHE systems. Formation of efficient yet ultra-light and flexible barriers to environmental elements is an inherently paradoxical task. For improving reliability of many FHE components, novel packaging is a must, especially for designs that contain copper or silver nanoink traces or adapted ICs that are sensitive to humidity and oxygen content in the air. Therefore, flexible, low-cost, easy to apply, and chemically stable packing materials that have sufficient thermal conductivity are needed for FHE development. Such efforts are underway, but

are still in early phases, with no single material that can answer all requirements at once. Packaging materials that can satisfy these complex requirements are not just useful for FHE systems. They can also be applied to many other fields such as conventional stand-alone RFIC tags, sensors in traditional applications, and biomedical devices that require efficient barriers against environmental factors.

7.7 General Outlook in next 25 Years

The question of how the next 25 years will unfold for FHE is a very complex one for several reasons. The technology is extremely heterogeneous and most parts being integrated are not mature on their own or capable of outperforming conventional alternatives. What injects hope to this seemingly pessimistic outlook is the fact that the best current technologies (i.e., CMOS and recent inorganic semiconductor technologies) are not always able to adapt to new requirements in form factor, power, and scaling, are very expensive to operate in the long run, and are intrinsically limited on the newer applications. Hence, FHE systems may still become a competitor as long as they challenge the established inorganic (CMOS) technologies on the correct applications. Such correct applications may include displays and lighting; energy generation, conversion, and storage; sensors and smart devices; logic and memory components; touch panels (human-machine interfaces), RF, and Wi-Fi networked devices (internet of things); medical devices; and many more.

Novel form factors, which enable or enhance performance, portability, durability, and many other aspects of conventional electronics, are sought by both civilian and military consumers. As with modern computing applications, making devices smaller, lighter, and more energy efficient are some of the goals of FHE. The U.S. Air Force has demonstrated interest in the following FHE application areas: human systems and cognition; embedded electronics for intelligence, surveillance and reconnaissance (ISR) and electronic warfare (EW); integrated power for autonomous operations; and survivable electronics. Given the variety of desired applications and their requirements, what seems of utmost importance is to understand the failure mechanisms of the materials and devices, especially in harsh environments, and the standardization requirements for interfaces and testing procedures.

Based on established trends, recent forces at play, and technological possibilities and strategic alignments, general trends for FHE technologies in the next 25 years may be outlined as follows.

7.7.1. Short Term (2015-2022): 1st Generation FHE Systems and Products

The next five years are extremely important for establishing a viable market and critical toolsets for FHE technologies, especially for defense/military applications. Following the 1980's MEMS development analogy, FHE must come up with digital-mirror-device-like killer products that solve unique problems in the defense domain.

Early FHE technologies in this phase will be dominated by novel packaging solutions and enabling toolsets for efficient, low-cost assembly of FHE devices, including 3D IC integration. In this sense, CMOS is not a rival but a complementary aide for FHE development. Similarly, CMOS may benefit from the surge of FHE applications, since slowing down of scaling may limit the conventional market expansion that CMOS has had for four decades.

Another characteristic of this early phase of product development is that both user market and defense technology will have room for error, with some start-up companies becoming prominent

already. It is expected that there will be critical acquisitions by big players (Intel, Phillips, Sony, etc.) preying on FHE start-ups to get ready for fast expansion in the medium to long term.

Application examples:

- Compact integrated sensor chips on flexibles substrates, transfer-printed devices from CMOS chips developed for smartphone sensor hub assemblies: crucial for many applications.
- Flexible lighting, illumination or signage products, and mini displays: easy entry to consumer markets.
- Flexible ultra-wide band and directional antennas: crucial for many applications.
- Passive RFID tags integrated with a single BioNano sensor: entry to medical markets.
- Graphene/CNT-based supercapacitors that can provide edge on energy harvesting.

Strategic materials:

- Higher conductivity and temperature resistant polymers than are currently available.
- Low-cost polymer composites based on carbon-based (graphene/CNT), metallic nanoparticles, and semiconductor nanowires.

Strategic fabrication tools:

- Printing systems combining multiple *high-resolution* (down to 1 micron) & *large-area* (up to several inches) deposition approaches so that both high quality sensors and transistors can be made in the same tool as large area displays or batteries in one pass.
- High resolution embroidery systems for e-textiles.
- Compact, flexible polymer packaging solutions for novel FHE integration and heterogeneous solutions.

7.7.2. Medium Term (2022-2030): Mature FHE systems and products

Established FHE products by high-profile companies in profitable product segments are the most significant markers of this period, especially on the defense side and certain consumer products (toys, vehicular electronics, wellness products, daily accessories, and so on.) Consolidation of successful companies into larger ones, especially in product segments that show greater market viability, is to be expected. Similarly, maturing fabrication technologies and growing expertise in FHE assembly should lead to standardization and even lower-cost manufacturing. Since CMOS can and will lower the cost of products at the perceived end of conventional scaling during this period, it will be necessary for FHE systems to retain their low-cost while also offering more capable systems with a higher level of integration. Thus, this middle phase will have less room for error and more demand for low-cost products. Although FHE systems may still not beat custom-built IC technologies, they will become more capable due to increasing levels of transfer printing and heterogeneous integration.

Going beyond *low-hanging fruit* applications, the FHE market will also see more differentiation between consumer and defense products in terms of cost and capabilities. For defense markets, drivers may include more secure communication protocols, higher power efficiency and peak

power levels, whereas civilian markets are likely to focus on lower-cost products and integration on wearable e-textiles as the *internet of things* market expansion reaches a peak. Moreover, the medium term will also see greater integration of FHE with photonics, in addition to displays and solar cells, including full-scale optical networks on wearables. Therefore, in many ways FHE systems will expand in this period much like the MEMS expansion in the early 2000's, fueled by smartphones and vehicular technologies.

Application examples:

- Active RFID tags/cards with sophisticated (multi)sensor banks & greater autonomy with artificial intelligence, blurring the boundary between today's RFID devices and full-scale FHE systems.
- 10 mW Energy Harvesting Chips: crucial for continued expansion of FHE products in both military and civilian domains.
- Novel THz devices and systems integration on flexibles, bringing the best of III- V/CMOS integration to address existing 'THz technology gap' for sources and sensors.
- Inflatable pads, pods, and unfolding structures (e.g., field hospitals) with complete operational infrastructures already assembled using existing FHE systems that would be of great interest especially to defense and space applications.
- 'Artificial skins' or 'adaptive sensors' for squad/crew in harsh environments: defense / space applications. These will have extensive physiological stress and mood-monitoring systems integrated with vehicular control, and team performance enhancement: going beyond simple state sensing and monitoring and becoming 'responsive' or 'actively correcting' tools.
- Large interactive surfaces for "info-taintment" in public spaces, malls, and living quarters of upscale homes.

Strategic materials:

- Highly-engineered, stable, low-cost multifunctional nanoinks based on multi-shelled metal nanoparticles and semiconductor/metal shelled structures.
- Multifunctional polymer/nanoparticle blends for photonic applications that allow higher integration of organic photonics with FHE applications.

Strategic fabrication tools:

- Printing systems combining high-resolution inkjet (down to 1µm) and ultra-compact 3D printing capabilities in a single head.
- Printing systems combining multiple additive and subtractive deposition techniques on the same platforms with six degrees of freedom (3 for sample and 3 for printing head).
- Digital-weaving systems for e-textile: custom weaving & embroidery of e-textiles for a given electronic design directly from schematics.
- Accurate multi-scale modeling and mixed-signal design software that have large and reliable databases for materials and devices that will enable designers to pursue new and exciting FHE systems.

7.7.3. Term (2030-2040): Intelligent and Agile FHE Systems

Heavily influenced by post-silicon (post-Moore) developments in the 2020's, FHE technologies will now become the mainstream. This phase is characterized by the emergence of highly capable FHE systems that are no longer driven by fabrication, packaging, and assembly techniques, but more by the peak power and data throughput they can handle. Empowered with novel multifunctional inks and complex nanomaterials developed in the medium-term phase, it will become possible to directly print extremely capable CMOS devices that can now challenge silicon-CMOS circuits in most low-power and low-cost applications. In fact, the division between conventional and flexible-hybrid systems will become blurred as FHE become more capable and dominant overall.

In this final period of FHE expansion, FHE may also make a large impact on computing. New computing paradigms based on reconfigurable low-cost FHE hardware and swarm intelligence may result in local, dynamically reconfigurable computer architectures that can have variable problem solving capabilities depending on the scale of the problem. Eventually this may become ad-hoc local 'cloud-like' computing solutions without remote servers that may be neither accessible nor safe. In this localized 'fog' computing, much can work like cloud computing except that resources are entirely local and more distributed around a house or office, as a user can take advantage of many low-cost FHE computing nodes.

On the biomedical front, after the initial (short-term and medium-term) phases where the focus was in diagnostics and therapeutics, the greater impact of FHE will be felt in *preventive care*. FHE systems will not be necessarily 'chasing' diseases, but will be used to prevent them by sophisticated wearable 'medical vests' that can assume greater autonomy, possessing vast numbers of sensors and computing resources to offer a reliable evaluation of immediate and foreseeable risks for the user. These medical vests may become the 'field' companions in the 'personalized medicine' paradigm and be programmed with personal medical data and direct connection to medical professionals. In the case of defense assets and emergency first responders, they can also possess a number of emergency drugs and analytical tools such as lab-on-a-chip patches to offer therapeutic features in high-risk patients or crews.

Application Examples:

- Truly flexible and low-profile energy harvesting FHE systems with peak power at ~100 mW and high capacity (~1,000mAh) comparable to today's AAA/AA class batteries.
- Specialized environments with built-in electronics and intelligence, such as inflatable space stations, pods, and/or team/crew suites with integrated electronic systems.
- Multi-functional and intelligent low-cost 'active' surfaces utilizing energy harvesting, sensing, and information displaying capabilities.

Strategic materials:

- Novel sol-gel based inks: complex multi-functional inks that can form a large variety of thin films using advanced sol-gel chemistry where the active ingredient can be chosen depending on the target material needed. This may become preferred.
- Printable tissues and cells for integration of FHEs with biomedical implants, and prosthetic limbs with active sensing and responsive surfaces.

Strategic fabrication tools:

- Stand-alone 'FHE Integration Stations": novel printed/flexible electronics fabrication and development environments similar to 'desktop' publishing in the 1990's, utilizing a variety of materials (3D printed plastics, solutions, inks, yarns, and so on) and surfaces (plastics, textile, and paper).
- Sophisticated design software with exhaustive libraries for materials, devices, and circuits that will firmly integrate multi-scale, multi-physics simulators and design tools with bio-electro-mechanical testing stations in a closed-loop. Such tools, or *R&D agents*, can develop novel materials based on specifications provided using artificial intelligence and can reduce the cost of developing and prototyping FHE systems even further.

7.8 The FHE Industry

Although there are other earlier and local bodies formed to promote and unite flexible electronics manufacturers and proponents in the U.S., FlexTech Alliance has recently emerged as the key industry body in the U.S. that vouches for FHE development and expansion, bringing together a number of other academic, federal, and private entities with otherwise divergent yet strong interest in flexible electronic systems. *FlexTech Alliance identifies itself as the premier industry association that advocates for the FHE Industry to build awareness within stakeholder communities about FHE and the impact of the technology on products and markets, providing R&D Funding and organizing conferences, workshops, webinars, and other networking opportunities for industry and customers.* It considers that FHE will make significant impact in the next five years on the consumer market along with defense applications, including:

- Medical/Pharmaceutical suppliers: 1st responder, military, telemedicine/home health care, product integrity, and security
- Sporting goods companies: fitness & active living, lifestyle monitoring
- Food packaging industry: Product tracking, ID and integrity/security

In a recent presentation [797], FlexTech Alliance has indicated that it expects future growth in the *power (batteries & PV)*, *sensors (defense, health & medical, infrastructure),* and *communications* (*signage, displays*) industries in particular. It informs that, according to a poll conducted among member companies (see Figure 113), 55% of them believe that within 3 years FHE will become widely integrated into commercial products. This figure raises to 90% within 5 years. Hence, this figure lends support to the time periods used in the short, medium, and long term projections introduced above.

Figure 113. FlexTech Alliance [797]

7.9 Standards Impacting FHE Development

All technologies applicable to FHE systems are rapidly evolving and incorporate extremely diverse devices and components. While this makes standards development more demanding, it also makes the development of standards all the more necessary. Several standards are being developed by the international and professional organizations regarding the design and operation of FHE systems [843]:

- IPC published three standards that related to FHE system development:
  - IPC/JPCA-4921 Requirements for Printed Electronics Base Materials and
  - IPC/JPCA-4591 Requirements for Printed Electronics Functional Materials.
  - IPC/JPCA 2291 Design Guidelines for Printed Electronics.
- IEC TC119 Printed Electronics Standards Technical Committee has established several Working Groups, as well as Ad-hoc Groups to identify potential standards topics. Also, TC119 has involved other organizations to act as advisors during the development of standards, e.g. IPC and COLAE.
- IEEE maintains two device test standards:
  - IEEE 1620-2008TM Test Methods for the Characterization of Organic Transistors and Materials.
  - IEEE 1620.1-2012TM Standard for Test Methods for the Characterization of Organic Transistor-Based Ring Oscillators.

8.0 FLEXIBLE HYBRID ELECTRONICS INDUSTRIAL BASE TECHNOLOGY RISKS

There are certain risks that are common to the FHE industrial base. Every sector has its unique financial risks, but some technology risks may be applicable to specific FHE materials or manufacturing/design process sector technologies. FHE material technologies encompass conductive and semiconductive materials, dielectric materials, barrier materials and substrates. Manufacturing/design process technologies include pre- and post-processing, printing/ coating/deposition, metrology and design/consulting. For this discussion, devices and applications are considered in a separate category.

This section captures a snapshot of the large number of participants in the FHE industry, including small and large businesses, R&D and manufacturing companies, and U.S. and international corporations. Section 8.1 through Section 8.3 include brief descriptions of a handful of FHE companies. These companies are actively involved in the development of many important building blocks for FHE technologies including active and metallic inks, materials and substrates, printing and assembly tools, design and testing expertise as well as consulting market analysis and research. The study team found that a number of companies disappeared from the market a few years after having entered it, either from acquisition by a larger firm, by making the decision to leave this market segment, or by failing altogether as a business.

Many companies were sent to the AFRL/RXME Industrial Base Information Center (IBIC) for an analysis of their financial, contracting, and intellectual property (IP) history. Analysis of this data is presented in Section 8.4. Table 43, Figure 114, Figure 115, Figure 116, and Figure 117 provide a summary and a visual depiction of the information received from IBIC regarding these companies.

8.1 FHE Devices & Applications Company Products

Several domestic companies that are producing or researching FHE devices and applications are summarized in Table 32. The FHE devices described in the table can be used for a variety of applications, ranging from flexible integrated circuits and batteries to wearables and displays. This list is simply a snapshot of a few companies that are involved in the FHE device market, and should not be considered exhaustive.

Table 32. FHE Devices & Applications Companies

Company	Headquarters	Unique Capability	Remarks
American Semiconductor, Inc. [980]	Boise, ID	Physically flexible integrated circuits and flexible silicon technology. FleX™ Silicon- on-Polymer is a proprietary post fabrication process that produces thinned silicon ICs (30-100µm).	Industry leader. Design team currently focusing application efforts on silicon-based flexible sensor systems.
Blue Spark Technologies [981]	Westlake, OH	Standard line of flexible batteries used in RFID, medical care devices, and RF enabled sensor systems. Developed a new ultra-thin battery series used in ISO thickness powered cards, transit tickets, and retail merchandising. TempTraq™ is a wearable Bluetooth thermometer that features a 24 hour primary battery cell.	IP acquired from Eveready Battery Company.
EM4 Incorporated [982]	Bedford, MA	Produce lasers, detectors, and high frequency receiver or transmitter electronics, including products for harsh environments.	Acquired by Gooch & Housego PLC (Somerset, UK) in 2011.
Enfucell Oy / Xymox [983]	Vantaa, Finland / Milwaukee, WI	Xymox Technologies has the exclusive license to produce, promote, and sell the SoftBattery® in North America. SoftBattery® is a thin, flexible, 1.5-6V eco- friendly power source.	Enfucell was spun off from Helsinki University of Technology.
i3 Electronics [984]	Endicott, NY	Electronics packaging and systems engineering company.	Created from bankruptcy of Endicott Interconnect Technologies in 2013.
Imprint Energy Incorporated [985]	Alameda, CA	Develops and manufactures flexible rechargeable batteries for wearable electronics. ZincPolyTM is a low cost, zinc-based rechargeable battery.	ZincPoly™ is not yet commercially viable.
MC10 Incorporated [986]	Cambridge, MA	Expertise in stretchable electronics. CHECKLIGHT™ is a wearable sensor for fitted head caps underneath sports helmets. Measures impact to the head. BioStamp is a stretchable sensor that monitors various medical and wellness factors.	Partnered with Reebok on CHECKLIGHT™. Collaborated with Army to incorporate technology into soldier uniforms.
MFLEX Incorporated [987]	Irvine, CA	Specializes in flexible circuitry and assembly. Product line comprised of thin flexible interconnect substrate fabrication and high density component assembly.	All production facilities in China, Singapore, Taiwan, and Korea.
MicroConnex Corporation [988]	Snoqualmie, WA	Specializes in flexible circuits and laser micromachining. Developed advanced flexible circuit technology including photolithographic patterning, alignment, and laser-drilling techniques.	
Nantero [989]	Woburn, MA	Uses CNTs for next-generation semiconductor devices, such as memory and logic. Primary development efforts CNT- based NRAM.	Lockheed Martin Corporation acquired Nantero's government business unit and has exclusive license for Nantero's IP.
SI2 Technologies, Inc. [990]	Billerica, MA	Product lines include antennas, arrays, and absorber systems.	
Solicore [991]	Redmond, WA	Develop embedded power solutions, including digitally printed batteries. Flexion product line includes ultra-thin, flexible, lithium polymer batteries.	
Thin Film Electronics ASA [992]	Oslo, Norway San Jose, CA	Produce printed electronics systems, including memory, sensing, display, and wireless communication.	Some development and production facilities in U.S. Only manufacturing facility in Pyongtaek, South Korea.
Uniqarta, Inc. [993]	Cambridge, MA	Ultra-thin, flexible chip assembly. Handle- Assisted Packaging technology uses industry standard pick-and-place equipment on thinned chips. Laser Enabled Advanced Packaging uses a laser actuation method.	

8.2 FHE Materials Companies

As demonstrated above in Section 3.0, materials used for FHE can be categorized into several different groupings, including conductive, semiconductive, dielectric, barrier, and substrate materials. The following sections contain lists of companies that are involved with each of these materials, specifically for FHE applications.

8.2.1 Conductive Materials Company Products

Several domestic companies that are producing or researching conductive materials for FHE applications are summarized in Table 33. The companies below produce a variety of conductive materials, including both organic and inorganic formulations. This company list is simply a snapshot of a few companies that are involved in the conductive materials market, and should not be considered exhaustive.

Table 33. Conductive Materials Companies

Company	Headquarte	Unique Capability	Remarks
Brewer Science [994]	Rolla, MO	Develops and manufactures advanced materials and equipment for fabrication of cutting-edge micro devices, including anti- reflective coatings, carbon electronics, multilayer systems, planarizing material, protective coatings, and thin wafer handling systems.	
C3Nano, Inc. [995]	Hayward, CA	Developing solution coated, transparent, conductive, CNT-based, ITO replacement materials technology.	
Cambrios [996]	Sunnyvale, CA	ClearOhm® is a coating material created from single crystal of silver NWs that produce a transparent conductive film through wet processing, with high optical and electrical performance for consumer electronic products.	
Creative Materials [997]	Ayer, MA	Electrically conductive adhesives, inks, and coatings, and dielectric and thermally conductive materials.	
Eikos, Inc. [998]	Franklin, MA	CNT-based transparent conductive coating technology for electrical and optical applications.	
Henkel Electronic Materials, LLC [999]	Irvine, CA	Produce highly conductive silver ink formulations, and adhesives for electronics and semiconductor assembly	Wholly owned subsidiary of Henkel AG & Co.
Intrinsiq Materials [1000]	Rochester, NY	Develops nanomaterial inks for the printed electronics industry. Nanoparticles can be smaller than 10nm, and are typically copper-based.	Sister facilities in Farnborough, England.
Nano-C [1001]	Westwood, MA	Produces fullerenes, nanotubes, and their chemical derivatives.	
Plextronics, Inc. [1002], [1003], [1004], [1005]	Pittsburg, PA	Develops, manufactures and sells conductive polymers and inks for use in organic electronics applications.	Spin off from Carnegie Mellon University. In 2014 Plextronics was sold to Solvay America.
Protavic America [1006]	Londonderry, NH	Manufacturer of high-performance conductive and insulative adhesives, encapsulated resins, sealants, coatings, and impregnation materials.	Subsidiary of Protex International located in France. Sites in U.S., France, Korea, and China.
Raymor Industries, Inc. [1007]	Quebec, Canada	Producer of high graphitized SWCNT produced through a patented plasma process. Supplier of electronically pure metallic and semiconducting SWCNTs and graphene.	Raymor Nanotech developed at the National Research Council Canada and the University of Sherbrooke. Acquired NanoIntegris, a spin off from Northwestern University.
Sun Chemical Corporation [1008]	Parsippany, NJ	Provides printing inks and resists used for manufacturing printed circuit and wiring boards.	Subsidiary of Group Coöperatief U.A. in the Netherlands
SouthWest NanoTechnologies (SWeNT) [1009]	Norman, OK	Supplier of single-wall, few-wall, and multi-walled CNTs.	Spin off from University of Oklahoma. Partner with Sigma- Aldrich for product distribution.
T-Ink [1010]	New York, NY	Produce conductive ink and smart electronics products.	
Vorbeck Materials [1011]	Jessup, MD	Produce graphene nanomaterial and conductive, graphene-based ink used to print electronics, such as RFID tags.	Developed by Princeton University professors.
XG Sciences [1012]	Lansing, MI	Manufactures and sells graphene nanoplatelets and develops engineered materials based on nanoplatelets.	Developed by Drzal research group at Michigan State University. Some IP licensed from MSU.

8.2.2 Semiconductive Materials Company Products

Several domestic companies that are producing or researching semiconductive materials for FHE applications are summarized in Table 34. This company list is simply a snapshot of a few companies that are involved in the semiconductive materials market, and should not be considered exhaustive.

Table 34. Semiconductive Materials Companies

Company	Headquarters	Unique Capability	Remarks
EMD Performance Materials [1013]	Philadelphia, PA	Develop advanced materials for existing and next generation display, lighting, and PV applications, including liquid crystal, LED, and OLED materials.	North American subsidiary of Merck KGaA (Darmstadt, Germany). U.S. manufacturing site in Savannah, GA.
Meliorum Technologies [1014]	Rochester, NY	Specialize in the commercialization of gold and silicon nanoparticles, as well as zinc oxide nanoparticle, cerium nanoparticles, metal & oxide nanoparticles and engineered nanofluids.	
NanoGram Corporation [1015]	Milpitas, CA	Manufacturer of inorganic nanomaterials, coatings and films, including silicon-based nanoparticles and silicon nanoparticle inks for printed electronics.	Wholly owned subsidiary of Teijin Group, Japan.
Next Energy Technologies, Inc. [1016]	Santa Barbara, CA	Develops organic photovoltaic devices with transparent, solution-processed small molecule OPV materials that can be printed as an ink in a low-cost roll-to-roll process.	Spin off of the Institute for Energy Efficiency at the University of California, Santa Barbara.
Nth Degree Technologies Worldwide, Inc. [1017]	Tempe, AZ	Developed printing methods and semiconductor device inks to create the world's only fully functional printed semiconductor products.	
Polyera Corporation [1018]	Skokie, IL	Develops flexible transistor technologies that enable novel electronics form factors and advanced electronics manufacturing processes.	Manufacturing facility in Taipei, Taiwan.
Sigma-Aldrich [1019]	St. Louis, MO	Products applicable to FHE include materials for OPVs, OLED/PLEDs, organic FETs Photonic and optical materials, printed electronics materials, liquid crystal materials, and micro/nano electronics materials and products.	Projected to be acquired by Merck KGaA, Germany.

8.2.3. Dielectric Materials Company Products

A couple domestic companies that are producing or researching dielectric materials for FHE applications are summarized in Table 35. Since dielectric materials are not used as often in FHE as conductive or semiconductive materials, only two companies are represented in the list below. While this list should not be considered exhaustive, it does represent two of the leading companies for dielectric materials in the FHE marketplace.

Table 35. Dielectric Materials Companies

Company	Headquarters	Unique Capability	Remarks
DuPont Microcircuit Materials (MCM) [1020]	Research Triangle Park, NC	Product lines include hybrid circuit materials, low temperature co-fired ceramic materials, passive component materials, PV metallization pastes, and printed electronic materials, including conductive copper inks.	Division of DuPont; Wilmington, DE.
Engineered Materials Systems [1021]	Delaware, OH	Manufactures printed electronics materials, including acrylics, epoxies, silicones, and urethanes for circuit board assembly, LED assembly, thermally conductive materials, encapsulants, negative photoresist, electronically conductive die attach, custom formulations, and potting compounds.	Wholly owned subsidiary of Nagase & Co. Ltd., Japan. Engineered Conductive Materials (ECM) functions as a separate entity and is a brand of Engineered Materials Systems, Inc.

8.2.4. Barrier and General Materials Company Products

One of the leading challenges for the FHE industry is the lack of barrier and encapsulation materials that are appropriately flexible as electronic devices conform to a variety of shapes. Therefore, only one company that supplies barrier materials specifically for FHE applications is represented below in Table 36. Of course, this list should not be considered exhaustive because of the volatile nature of the FHE market in general, but significant research will need to be performed to address this existing gap in FHE technology and enable more industry players in the barrier material domain.

Table 36. Barrier and Other Materials Companies

Company	Headquarters	Unique Capability	Remarks
Universal Display Corporation [1022]	Ewing, NJ	Focuses on OLED technologies and materials for full-color displays, lighting products, flat panel displays, and organic electronics.	Currently working with DOD and DOE.
Vitriflex, Inc. [1023]	San Jose, CA	Produce barrier technology, a polymer film with an all-inorganic barrier stack that utilizes a proprietary roll-to-roll technique to produce high- performance flexible electronics.	Formed partnerships with Henkel (Germany) and Kuraray Co. Ltd. (Japan).

8.2.5. Substrate Company Products

Several domestic companies that are producing or researching substrate materials for FHE applications are summarized in Table 37. Since a significant portion of FHE technologies can use paper and plastic substrates commonly used in several other industries, a large number of companies exist that produce these substrate materials. However, the companies listed below reflect ones that are specifically targeting the FHE industry for their substrate materials. This company list is simply a snapshot of a few companies that are involved in the FHE substrate market, and should not be considered exhaustive.

Table 37. Substrate Companies

Company	Headquarters	Unique Capability	Remarks
CoorsTek [1024]	Golden, CO	Produce thick and thin-film substrates, microelectronic and sensor components, and parts for pick and place techniques.	Manufacturing facilities globally with many in the U.S.
DuPont Teijin Films [1025]	Chester, VA	Producer of PET and PEN films for flexible circuits, membrane touch switches, capacitors, RFID, motor film, flexible electronics, wire and cable, and casting and release.	50:50 global joint venture between DuPont and Teijin.
ENrG, Inc. [1026]	Buffalo, NY	Produce Thin E-Strate®, an ultra-thin, flexible, fully- dense zirconia-based ceramic substrate that is flexible for roll to roll processing and compatible with compact and curved designs.	Technology licensed from Corning.
Polyonics, Inc. [1027]	Westmoreland, NH	Leader in polymeric coating technologies for high performance film, tape, and label applications. Manufactures clear and white top coated polyimide films for the printed electronics industry.	
Sheldahl (Multek) [1028]	Northfield, MN	Producer of flexible substrates and laminates to support the printed circuit, touch sensor, display, aerospace and defense industries.	Multek (Hong Kong) acquired Sheldahl in 2004.

8.3 FHE Manufacturing/Design Process Companies

As demonstrated in Section 4.0, many steps are involved in the process of designing and manufacturing FHE technologies, including component design, pre-processing methods, application methods, post-treatment processes, and metrology/quality control checkpoints. Companies involved in each of these manufacturing areas will be highlighted in the following sections.

8.3.1 Pre- and Post-Processing Company Products

Several domestic companies involved with pre- and post-processing techniques in FHE manufacturing are summarized in Table 38. Pre-processing involves ensuring that the substrate is ready to receive electronic materials, while post-processing techniques, such as sintering, enable the device to achieve its maximum performance. This company list is simply a snapshot of a few companies that are involved in pre- and post-processing methods, and should not be considered exhaustive.

Table 38. Pre- and Post-Processing Companies

Company	Headquarters	Unique Capability	Remarks
Adphos North America, Inc. [1029]	Milwaukee, WI	Near-infrared drying, curing and sintering systems for printed electronics, graphic arts, and industrial applications.	Subsidiary of Adphos Innovative Technology GmbH (Germany).
Enercon Industries Corporation [1030]	Menomonee Falls, WI	Surface treatment equipment for corona, plasma, flame and ozone pretreatments.	
NovaCentrix [1031]	Austin, TX	Offer photonic curing tools, powders, and inks, enabling development and manufacturing of the next generation of electronics devices.	
Xenon Corporation [1032]	Wilmington, MA	Designs and manufactures pulsed light systems for printed electronics sintering and UV curing.	

8.3.2 Printing/Coating/Deposition Company Products

Several domestic companies exist that are involved in applying functional materials to substrates through printing, coating, and deposition processes to create FHE technologies. As mentioned in Section 4.0, some of these printing, coating, and deposition processes have been used heavily in other industries for decades, so a large amount of companies perform this kind of work. While this list should not be considered exhaustive, Table 39 provides a description of a few of these companies that are specifically targeting FHE applications.

Table 39. Printing/Coating/Deposition Companies

Company	Headquarters	Unique Capability	Remarks
Advantech US [1033]	Pittsburgh, PA	Evaporating Printing™ process uses precision shadow masks combined with sub-micrometer registration and thermal, electron beam, and sputter deposition techniques to additively print sensors, circuits, and devices.	
ALD NanoSolutions [1034]	Broomfield, CO	Particle ALD™ creates chemically bonded nanocoating on ultrafine particles, through the use of fluidized bed reactors. Polymer ALD™ creates nanocoatings on polymer films, and plan to demonstrate continuous roll-to-roll	Spin off from ALD laboratories at the University of Colorado.
Applied Materials [1035]	Santa Clara, CA	Involved in roll-to-roll vacuum coating systems that deposit thin films for flexible electronics, packaging, and advanced technology, semiconductor, display, and solar applications.	Manufacturing in U.S., Europe, and Asia.
Deposition Technology Innovations (DTI) [1036]	Jeffersonville, IN	Contract vacuum coater of industrial, barrier, window, and reflective films, including roll-to- roll web sputter coating of optically clear, conductive films.	
E Ink Corporation [1037]	Billerica, MA	Develops electronic paper displays for various applications. Some displays can be mechanically flexible.	Spin-off from MIT Media Lab. U.S. subsidiary of Prime View International (PVI), Taiwan.
Frontier Industrial Technology, Inc. [1038]	Towanda, PA	Designs and manufactures custom-configured coating and converting machinery for many industries including microelectronics.	
Harper Corporation of America [1039]	Charlotte, NC	Specializes in laser engraved ceramic anilox roll production and restoration for gravure and flexographic printing markets.	Facilities in Depere, WI and Bangkok, Thailand
MesoScribe Technologies, Inc. [1040], [1041]	E. Setauket, NY	Developed Mesoplasma™ direct write technology that manufactures harsh environment sensors and structurally integrated electronics with high-precision and high throughput.	Technology developed under the DARPA mesoscopic integrated conformal electronics (MICE) program.
nScrypt [1042]	Orlando, FL	Manufactures, sells and services Sciperio's Micro Dispense Direct Write (MDDW) technology.	Founded as a joint venture between Sciperio and Spectra Technologies.
nTact [1043]	Dallas, TX	Develops advanced, high-precision slot die deposition coating systems for the display, microelectronics, alternative energy markets.	
Optomec [1044]	Albuquerque, NM	Produces an aerosol jet system, which is a non- contact direct write printing process capable of directly depositing a wide range of electronic materials onto various substrates.	
Sciperio Incorporated [1045]	Orlando, FL	Offer products and services in laser photonics, digital printing, airships, and antenna research.	
Sensor Films, Inc. [1046]	Rochester, NY	Proprietary inkjet-based deposition systems that pattern transparent conductive polymer films and create invisible conductive traces, with the use of conductive polymers, for application in flexible touch screen sensors.	
Voxel8 [1047]	Sommerville, MA	Developed 3D electronics printer that uses PLA as the matrix material and conductive silver inks.	Technology from Harvard University.

8.3.3 Design/Consulting Company Products

Several domestic companies involved in design and consulting for FHE technologies are summarized in Table 40. The companies below provide a wide range of services, including consulting for specific FHE applications, such as photovoltaics and displays, as well as consulting for large area electronics and printed electronics in general. This company list is simply a snapshot of a few companies that are involved in FHE design and consulting, and should not be considered exhaustive.

Table 40. Design/Consulting Companies

Company	Headquarters	Unique Capability	Remarks
Abbie Gregg, Inc. (AGI) [1048]	Tempe, AZ	Provides engineering and consulting services, with experience in photovoltaics, wafer fabrication, assembly multichip modules, flat panel displays, and flexible electronics start-up planning.	
Printovate Technologies, Inc. [1049]	Palatine, IL	Provides design services specializing in large area electronics.	
Soligie, Inc. [1050]	Mankato, MN	Design and manufacturing services for printed and flexible electronics.	Wholly owned subsidiary of Taylor Corporation.

8.3.4 Metrology Company Products

Metrology is an important step in the overall manufacturing process for FHE, but it is currently a technology challenge that needs to be addressed. One company involved with metrology tools for FHE is displayed in Table 41, but descriptions of a few others can be found in Section 4.1.4. Nevertheless, research needs to be performed to address the technology gap in metrology and quality control tools and processes for FHE technologies.

Table 41. Metrology Companies

Company	Headquarters	Unique Capability	Remarks
J.A. Woollam Co. [1051]	Lincoln, ME	Leader in spectroscopic ellipsometry. Developing an in-line version for roll-to-roll applications.	Spin-off from University of Nebraska.

8.4 Financial Risk

Overall financial risk for the Flexible Hybrid Electronics firms studied is fairly low. In addition to the 67 companies reported above, another 81 firms were analyzed, leading to a total of 148 companies that are generally connected with FHE materials and manufacturing. Of these 148 companies, eight were seen as high risk (5.4%), nine were evaluated as moderate risk (6.1%), 97 were ranked low risk (65.5%), and there was insufficient data to rate the remaining 34 (23.0%) companies. Table 42 lists the criteria used to evaluate company risk.

As seen from the company overviews, some of these FHE companies were new starts, but they also had healthy R&D funding. Others were firms long in the business (e.g. DuPont, Sheldahl) that had years of experience in other technologies and had a healthy business base to support their expansion into the FHE sector. In many cases the technologies they were experienced producing (e.g. thin films, inks) are directly adaptable to FHE developments, so the expansion into FHE product lines is a logical business development.

Table 42. Financial Risk Rating Criteria

Risk		Description
Low		Good to strong financial condition. Financial metrics are concentrated at the upper end of the scale. Economic forecasts show continued good to strong performance. Reductions in government contracts would have only a limited impact on viability.
Moderate		Financial condition is stable but sensitive to market conditions. Economic forecasts show relatively consistent performance with some possibility for significant change. Some management corrective action is warranted. Reductions in government contracts could have a negative impact on viability.
High		Financial condition is serious and may indicate a near-term bankruptcy. One or more financial metrics are at or below the critical stage. Market pressures could readily influence this entity. Government intervention is a possibility if a unique technology exists.

Risks were also calculated by FHE technology area, and the results are shown in Table 43.

Table 43. Financial Risk by FHE Technology Area

Technology Area	High	Moderate	Low	Insuff. Data	Total
Devices/Application	3 / 5.9%	3 / 5.9%	37 / 72.5%	8 / 14.0%	51
Printing/Coating/Deposition	3 / 10.3%	2 / 6.9%	16 / 55.1%	8 / 27.6%	29
Conductive Materials	1 / 3.8%	3 / 11.5%	14 / 53.8%	8 / 30.8%	26
Design/Consulting	0	0	8 / 72.7%	3 / 27.3%	11
Pre & Post-Processing	1 / 12.5%	0	5 / 62.5%	2 / 25%	8
Dielectric Materials	0	0	2 / 100%	0	2
Semiconductive Materials	0	1 / 11.1%	6 / 66.6%	2 / 22.2%	9
Metrology	0	0	2 / 66.6%	1 / 33.3%	3
Barrier Materials	0	0	3 / 100%	0	3
Substrates	0	0	4 / 66.6%	2 / 33.3%	6
Totals	**8 / 5.4%**	**9 / 6.1%**	**97 / 65.5%**	**34 / 23.0%**	**148**

A visual representation of the financial risk ratings provided by IBIC are provided in Figure 114. This graph was created using the number of companies that were categorized as high, moderate, and low risk for each technology area, as listed in Table 43.

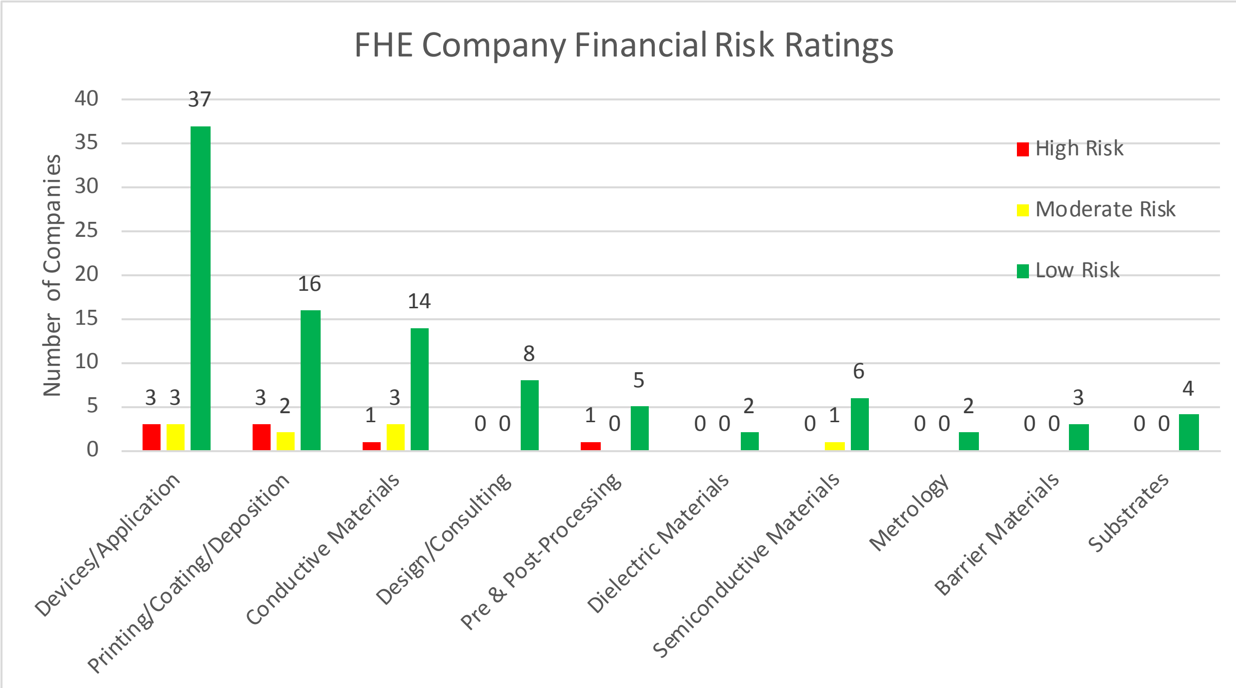

Figure 114. FHE Company Financial Risk Ratings

In addition to financial risk ratings, IBIC also provided information regarding the number of patents the company holds and the amount of government funding they have received, in an attempt to portray how involved the companies are in R&D efforts. Figure 115, Figure 116, and Figure 117 provide visual representations of this data. For everything except the company sales and the number of employees in Figure 115, the graphs are based on the total 148 companies analyzed and broken down above in Table 43. The company sales and employee data is based on a subset of 68 companies, since the additional data did not become available in time for the entire analysis.

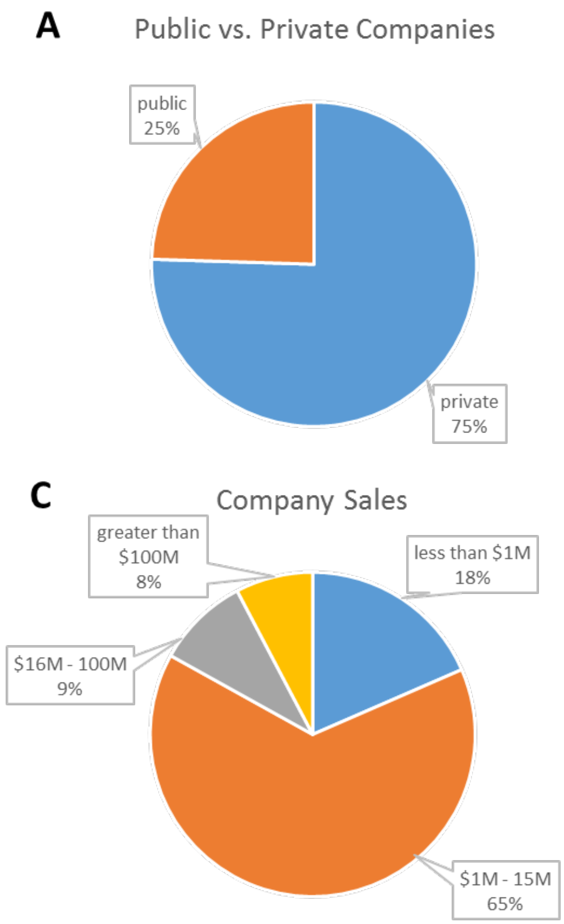

Figure 115. A, B, C, and D Represent Various Data for FHE Companies

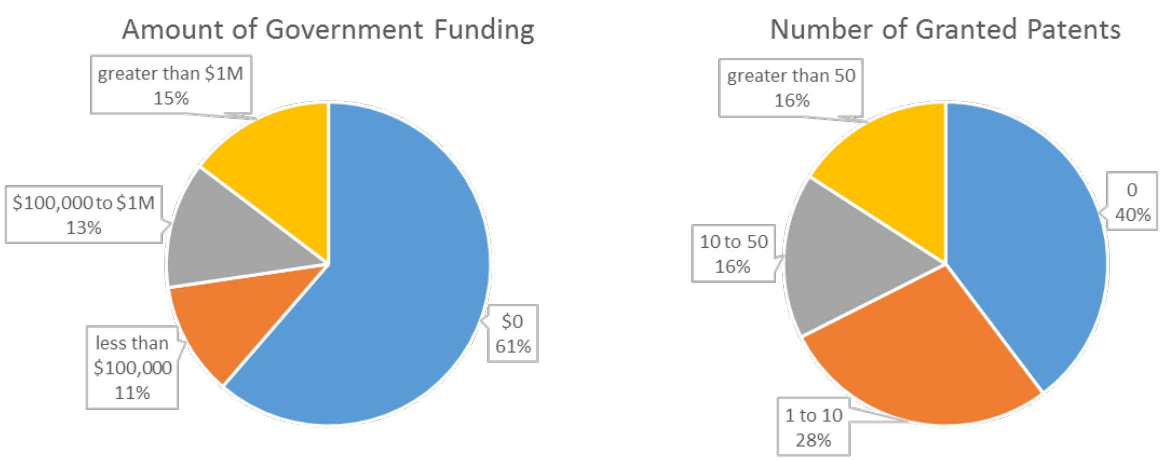

Figure 116. Representation of the Government Contract Funding and Granted Patents Each FHE Company has Received

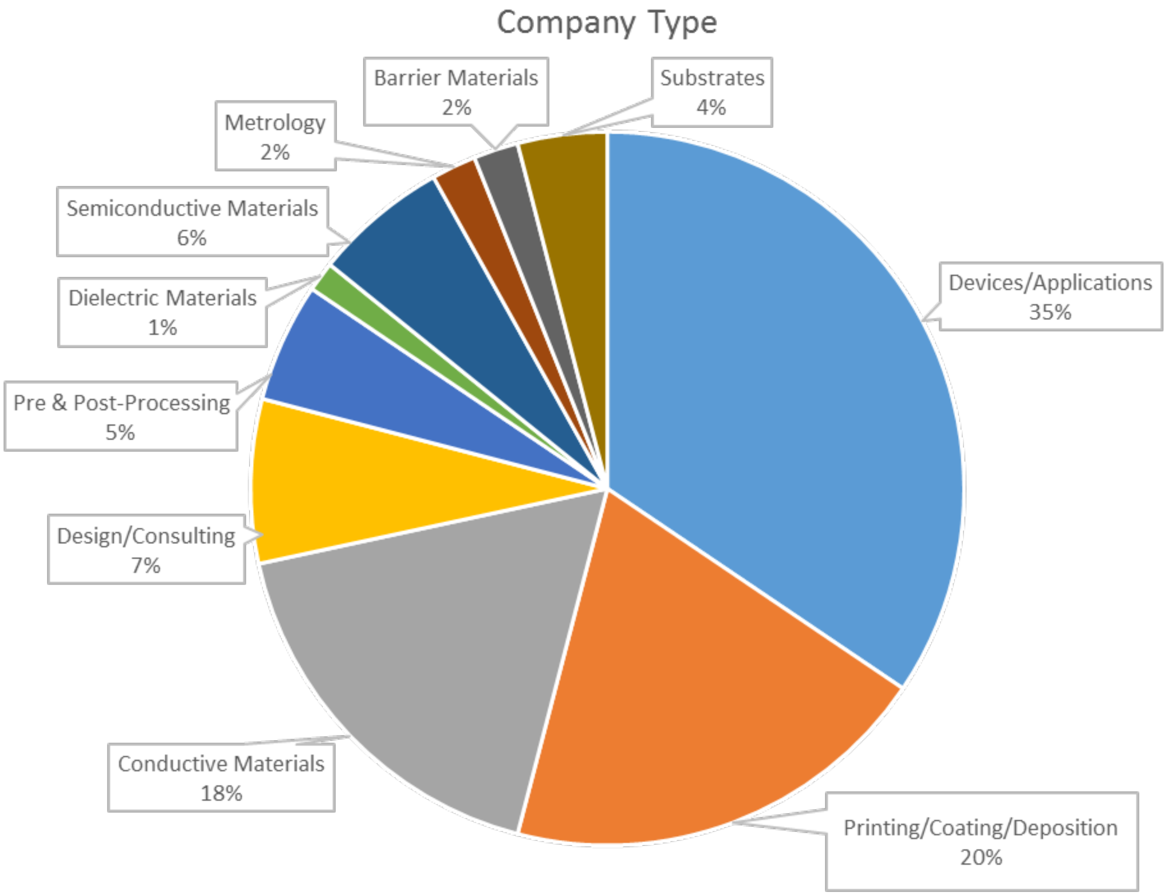

Figure 117. Representation of the Different Products Offered by FHE Companies

Through Figure 115, Figure 116, and Figure 117, various conclusions can be drawn regarding the FHE companies that were analyzed. First of all, a large majority of the companies are small, private organizations that have less than 50 employees and annual sales of less than $15 million. This is perhaps because many of the companies involved in the FHE industry are start-ups or spin-offs from universities looking to take advantage of the new but rapidly evolving technology space. However, somewhat surprising is that, despite their new and small nature, most of these companies have a low financial risk rating. The relatively large number of companies where the financial risk rating was not available is also most likely due to the new, volatile, and private nature of these companies.

Figure 116 demonstrates that while there is definitely a significant amount of companies that are not utilizing government funding or pursuing IP, a large portion of the analyzed companies are involved in these types of activities. This could be because FHE as a whole is still mainly an R&D effort, and therefore government funding is required to carry out such activities and the IP portfolio for this market still needs to be established. The large percentage of companies that are not investing in IP or government funding perhaps represent the relatively newer companies that are not yet in a position to pursue such activities.

Figure 117 represents the distribution of the different companies that were analyzed. However, this is not necessarily an accurate indication of the distribution of the various focus areas within the FHE industry as a whole.

8.5 FHE Industry R&D (Way Ahead)

The FHE industry is promulgating a number of technology advances in materials and processes. As with the conventional electronics industry FHE is moving toward smaller and finer pitch circuitry and development of flexible microcircuits using a greater variety of materials including carbon nanotubes (CNT), silver nanowire (NW), liquid crystal materials, organic photovoltaics, and alternative substrates. Improvements in FHE processing include a move to in-line and roll processing, 3D shape processing, printing on larger area substrates and advances in wafer scale processing. There is also a move to greater use of FHE processes for energy storage devices (batteries), photovoltaics, OLED lighting, and sensors. Specific examples are given below.

In 2013, Advantech US announced their ability to produce circuits and sensors with features of sizes as small as 5 microns using bulk metal, oxide, and semiconductor materials, producing components such as resistors, capacitors, and transistors embedded directly into conducting lines, reducing design complexity, size, and weight. The company originally proved the Evaporation PrintingTM process in a single chamber system, but it has recently developed and is testing the concept of flexible multi-chamber in-line manufacturing using their first-of-its-kind miniLineTM machine. This technology can use up to six masks and deposit up to six material sources per chamber without breaking vacuum. According to 2013 literature, the company is currently characterizing in-line manufacturability and scaling up the process; validating performance, throughput, yield, and cost assumptions; and identifying modifications needed for production level equipment. The next step in Advantech US' technology roadmap is to design and build a manufacturing tool for production. Their long term vision includes higher resolution output, production-level printing on flexible substrates, printing on large area substrates, and roll-to-roll manufacturing.

In 2011 at the Flexible Electronics & Displays Conference, American Semiconductor presented the industry's first demonstration of a wafer scale process for high performance, flexible, single crystalline complementary metal-oxide semiconductor (CMOS) circuits. Their technology, called FleX™ Silicon-on-Polymer, is a process that creates high performance, single-crystalline CMOS circuits with multi-layer metal interconnect on a flexible substrate. This proprietary FleX post-fabrication process can be applied to silicon-on-insulator (SOI) processes from any foundry to create flexible silicon wafers, with thicknesses less than 2000 angstroms, on top of a polymer substrate. In addition to the FleX™ Silicon-on-Polymer products, American Semiconductor also produces thinned silicon ICs that range from 30 – 100 µm in thickness.

In 2014, C3Nano showcased its new C3D™ technology at FINETECH, the world's leading conference and exhibition on Flat Panel Display. This technology is based on transparent conductors, but it can be formed into a variety of 3D shapes while still maintaining excellent optoelectronic properties.

Cambrios received a Small Business Innovation Research (SBIR) contract in 2005 from the DOD for the development of NanoWire (NW), but a target application for this NW development

was not specified. Additionally, in June 2010, Cambrios was selected by the Defense Advanced Research Projects Agency (DARPA) to be part of the Low-Cost Lightweight Portable Photovoltaics team, led by Ascent Solar Technologies, Inc. The goal of this project, which was to last approximately 4.5 years, was to demonstrate low-cost lightweight PVs that can withstand battle conditions and environmental extremes.

In May 2014, it was announced that DuPont MCM and the Holst Centre have extended their collaboration focused on advanced materials for the printed electronics industry. The collaboration is expected to advance technology specifically in the areas of OLED lighting, wearable electronics, in-mold electronics, sensors, and smart packaging. The work will concentrate on optimizing printed metallic structures on flexible substrates in terms of conductivity, fine line deposition, and low energy sintering. Several roll-to-roll compatible printing techniques, including screen, flexography, and inkjet, will be studied, and they will focus on alternative conductor metallurgies as well as reactive systems for depositing conductive traces.

In February 2015, EMD Performance Materials attended and presented at the 2015 Flexible and Printed Electronics Conference in Monterey, California. During their talks, they focused on EMD's lisicon® brand and on their liquid crystal materials. They described how their small molecule and polymeric organic semiconductor materials were ideal for flexible electronic applications because of their enhanced performance and processability. Additionally, they went into detail about their dielectric and organic photodetector materials and how they can be used for flexible electronics. They also discussed their liquid crystal materials and how they can be used to create flexible LCDs, as well as the benefits, negatives, and technical challenges of flexible LCDs in general. Their attendance and the topics of their talks demonstrate EMD Performance Materials' presence in the flexible electronics industry, and helps to provide insight into which of their products they feel will likely create the most value in flexible electronics applications going forward.

ENrG has one granted patent from 2012 for "operation of an electrolysis cell." They also have had two SBIR contracts with the Department of Defense, one in 2007 and one in 2009, for "Energy Storage Systems for Very High Altitude Very Long Endurance Solar Aircraft." In February 2015, Henkel Electronic Materials attended the 2015 Flexible and Printed Electronics Conference in Monterey, California. There they presented on two different topics – their new highly conductive silver ink formulations and the use of their inks in printed heater applications. In these talks they described how their new line of silver inks had higher conductivity values than their previous formulations, which allows for lower ink consumption and cost reductions for their customers. These formulations also provide increased flexibility in the end product because thinner conductor lines can be printed with these new inks. They then went on to describe how their new line of conductive inks, in combination with other electronic inks in their portfolio, could be used to create printed positive temperature coefficient (PTC) heaters for applications in automotive interiors, clothing, medical devices, lunch trays, stadium seating, and pools, among others. Henkel's new line of silver inks can be used in other printed electronics applications as well.

Intrinsiq Materials was awarded a contract in October 2014 through the U.S. Department of Energy (DOE) SunShot Initiative to "develop and commercialize an innovative method of using nickel silicide and copper in solar power cells." (The SunShot Initiative is a collaborative national effort that drives innovation to make solar energy fully cost-competitive with traditional energy sources before the end of the decade.) For this effort, Intrinsiq Materials will work with Rochester Institute of Technology and the State University of New York (SUNY) College of Nanoscale Science and Engineering Photovoltaics Manufacturing and Technology Development Facility to demonstrate that this technology can lead to printed solar cell contacts produced at lower prices and with greener manufacturing techniques.

MC10 has collaborated with the U.S. Army to incorporate flexible, lightweight electronics into soldier's uniforms for health monitoring and solar energy purposes. This addition aims to make the monitoring of soldiers' health completely wireless and also provide portable, rechargeable power to each individual. Additionally, MC10 Inc. has had 7 contracts with the U.S. Department of Defense. MC10 has been issued 5 patents since 2012, 4 of which are related to stretchable, flexible circuitry and electronics. Additionally, MC10 has 38 published patent applications which range from balloon and cardio catheter electronics to monitoring hit count for impact events.

MFLEX has been granted 16 patents for products ranging from stretchable circuit assemblies to slot core transformers. They also have 9 patents pending for stretchable circuit assemblies, miniature circuitry and inductive components and their respective manufacturing methods.
Nano-C had several SBIR and Small Business Technology Transfer (STTR) contracts between 2004 and 2010 from the National Science Foundation (NSF) and DOE. These contracts involved scale-up of CNT synthesis, synthesis of long CNTs from waste plastics, using fullerene materials in flash memory development, purifying CNTs to metallic or semiconducting forms, and high-efficiency, stable, and high performance OPV devices.

In February 2009, before Teijin acquired NanoGram Corporation, Teijin formed a technology development agreement with NanoGram Corporation to optimize their silicon particles and inks and also to develop a processing technology that would allow for a silicon nanoparticle film to be sintered at temperatures below 200 °C. As a result of this agreement, Teijin and NanoGram Corporation announced the successful fabrication of the first TFT produced by ambient printed nanosilicon to reach a carrier mobility of 2.0 cm2/Vs. The printable silicon material was based on nano-scale crystalline silicon particles formulated into inks, which can be ink-jetted or spin-coated onto a substrate. In NanoGram's patent application for similar technology, the ink formulation is simply described as the silicon nanoparticles dissolved in an organic solvent.
Nantero is the first company to develop microelectronic-grade CNT materials and to actively develop semiconductor products using CNTs in a production CMOS fab. Nantero's primary development is NRAM, a high density fast nonvolatile RAM based on CNTs, and Nantero intends for it to replace all existing forms of memory.

Next's technology consists of an entirely new generation of transparent, solution-processed small molecule Organic Photovoltaic (OPV) materials that can be printed as an ink in a low-cost roll-to-roll process to create solar cells. The small molecule semiconductor technology overcomes the limitation of earlier generations of polymer-based organic thin-film solar technology by allowing

for improvements in scalability, stability, and efficiency, which ultimately leads to product lifetimes and conversion efficiencies that are competitive with conventional solar technology. In March 2014, it was announced that Next Energy Technologies had been awarded two separate SBIR Phase II grants totaling $1.75 million. The DOE granted $1 million as part of its strategy to accelerate clean energy innovation. NSF also granted Next $750,000 to support the R&D of new materials and devices to increase the power conversion efficiency of Next's OPV technology. NthDegree invented a ground-breaking new method of transferring specific semiconductor properties to a substrate using a printing process and proprietary inorganic semiconductor inks. Their inks are comprised of microscopic functional semiconductor devices (e.g. diodes, transistors), which are built using traditional wafer fabrication technology. These semiconductor-containing inks are printed using standard high-speed printing presses, and are then converted into final products. By creating functional electronics through printing processes, NthDegree can bypass the traditional semiconductor processes, which allows them to be an extremely low cost, state-of-the-art producer. Additionally, printing, as opposed to traditional semiconductor processes, enables a variety of form factors, functionality, and additional features. These semiconductor device inks and printing processes are the base technology for all of NthDegree's products, which include printed solid-state lighting and printed photovoltaics.

NanoIntegris, acquired by Raymor Industries, is the world's leading supplier of electronically pure metallic and semiconducting SWCNTs and graphene. NanoIntegris separates and purifies nanomaterials by their optical and electrical properties, a process called density gradient ultracentrifugation (DGU) developed by the Hersam research group. This process involves dispersing the nanomaterials into an aqueous solution using a combination of surfactants, causing the different surfactants to selectively bind to the different types of nanomaterials. Then the mixture is centrifuged under a very high relative centrifugal field which causes the various types of surfactant-encapsulated nanoparticles in the solutions to separate into layers due to their differing densities. These separate layers can then be isolated using conventional chemical methods.

Sensor Films is initially focusing on flexible touch screen sensors, but plans to address other printable electronic devices and systems in the future, specifically in the consumer, industrial, and medical device markets. They envision that their low cost systems and solutions will help to enable the IoT. Sensor Films has promised to unveil in the near future their family of equipment that provides a means for mass production of the next generation of flexible, low cost devices. Current plans call for the delivery of a sheet-fed digital deposition system configurable to customer production demands during the second half of 2015. Additionally, a high volume, in-line roll-to-roll digital deposition system is under development and will be available in 2016, according to Sensor Films' officials. In November 2015, Sensor Films announced a new manufacturing platform for high throughput digital deposition of decorative and functional materials on various substrates.

In 2013, Solicore was able to create the world's first digitally printed battery. Today, Solicore is a worldwide leader of embedded power solutions, offering its Flexion product portfolio of ultra-thin, flexible, lithium polymer batteries for powered cards, RFID, and micro medical devices. Solicore also provides technology integration services that enable customers to accelerate their time to market and increase product design efficiencies. Solicore was awarded a contract in 2003

by the U.S. Army's CECOM department for the development of rechargeable lithium polymer batteries, intended for the Army's Land Warrior program among other potential applications. A key hurdle to overcome in the production of flexible electronics is providing a means of blocking moisture and oxygen without using glass, an inflexible material. Vitriflex takes a unique approach to this problem, using polymer film with an all-inorganic barrier stack that utilizes a proprietary roll to roll technique to produce high-performance flexible barrier films.

Voxel8 has developed a 3D printing platform that is capable of printing functional materials. Compared to currently available desktop 3D printers that create parts from a single material (typically thermoplastic materials or UV resins), the Voxel8 3D printer can co-print matrix materials such as thermoplastics, and highly conductive silver inks. This allows for the creation of customized electronics devices, with the option of the electrical components being embedded within the 3D printed structure. Voxel8 identifies devices such as 3D printed antennas, electromagnetic coils, stack ICs, and quadcopters (their demonstration product) that can be printed with their technology, but ultimately the designs are limited only by the system's innate capabilities and the user's imagination. Voxel8's 3D Electronics Printer offers a variety of features that set it apart from other 3D printers, besides the ability to print electronics within a 3D printed structure. These features include pneumatic room-temperature dispensing, autobed leveling, a highly repeatable kinematic coupled bed, and an interchangeable ink cartridge system. The onboard pneumatic dispense system allows for high precision, direct-writing of functional inks and other matrices. The build plate is auto-leveled using distance probes at multiple points, so the user does not have to worry about an idle cartridge coming in contact with the part during printing. The kinematically coupled bed enables easy insertion of electronic components by removing the bed during the print process, inserting the component of interest, and then continuing the printing process right where it left off. The interchangeable cartridges allow for combinations of various matrix materials and conductive inks into a single 3D print job. The printer includes a large 4.3" touch screen display that guides component placement and orientation during printing. The overall design of the printer allows for the user to observe parts as they are printed.

TECHNOLOGY GAP: FLEXIBLE HYBRID ELECTRONICS INDUSTRY

Manufacturing for U.S.-developed FHE technologies are often outsourced to other countries, while governments from the European Union, Singapore, Japan, Korea, and China continue to invest in enabling technologies for FHE.

POTENTIAL SOLUTION

The U.S. FHE Manufacturing Innovation Institute could help foster U.S. leadership not only in research and development but in commercialization within this emerging industry.

TECHNOLOGY GAP: FLEXIBLE HYBRID ELECTRONICS INDUSTRY

FHE systems are developed and consumed in a global market, which implies that U.S. companies often collaborate with and are purchased by foreign entities, creating the potential for counterfeit or malicious technology to enter the supply chain.

POTENTIAL SOLUTION

Leverage the processes already in place in related industries (e.g. aircraft manufacturing) for compartmentalizing technology information and for identifying and managing trusted sources.

TECHNOLOGY GAP: FLEXIBLE HYBRID ELECTRONICS INDUSTRY

A significant number of firms involved in the photovoltaics business are failing, indicating that this is still a risky technology investment. Similar trends can be observed with other technology areas within FHE.

POTENTIAL SOLUTION

Government direct investment through agencies such as DARPA, the service laboratories, academia, and the Title III Program can help to determine the most promising new players in the FHE marketplace.

TECHNOLOGY GAP: FLEXIBLE HYBRID ELECTRONICS INDUSTRY

The lack of a well-developed supply chain and deep infrastructure is leading to FHE products that are not cost competitive compared to the incumbent technology.

POTENTIAL SOLUTION

Enhanced research efforts by entities like the FHE Manufacturing Innovation Institute can help to accelerate the development and commercialization of critical materials, processes, equipment, and tooling.

9.0 CONCLUSIONS AND RECOMMENDATIONS

The FHE industry currently comprises a number of companies that have proposed or are producing a diversity of technologies that together enable FHE. As these enabling technologies continue to improve and the industry continues to integrate, FHE is expected to grow into a key technology sector with numerous application areas in both civil and defense markets. While currently there is a rather distinct separation between conventional electronics and FHE, the line between these two technologies is expected to fade over time as FHE becomes more capable and FHE materials and manufacturing technologies become more cost effective, possibly even for electronics products that are traditionally made using conventional technologies.

Despite current shortcomings, FHE is growing steadily in capabilities and applications. While forecasts are widely varying, it is clear that FHE will continue to expand rapidly. The adaptation of conventional (e.g., CMOS) electronics to flexible substrates will enable FHE use in applications beyond those possible with conventional electronics, without sacrificing performance. However, before FHE can become pervasively successful, the industry must deal with challenges and opportunities that include thermal management; resilient, flexible substrates; limited power supply and physical space; 3D integration; photonics integration; and flexible packaging.

This section presents conclusions and recommendations specifically for FHE technologies, but some statements can apply to the electronics industry as a whole. For each item, it is obvious from the context whether it addresses just FHE, or electronics in general. A number of the conclusions and recommendations regarding FHE are inspired by those documented by iNEMI in its 2015 Roadmap chapter on Large Area Flexible Electronics (LAFE), enhanced if necessary to address FHE instead of just LAFE and to consider the additional requirements of military applications. All conclusions and recommendations regarding the electronics industry status, challenges, and opportunities are separated below into several categories, for ease of discussion and further analysis.

9.1 General

1. The FlexTech Alliance, which won the government contract award for the FHE Manufacturing Innovation Institute, has chosen the name NextFlex for the institute. NextFlex is surveying its members and the attendees to its Flexible Electronics (FLEX) conferences with the understood purpose of starting to create roadmaps for optimally guiding its efforts. NextFlex members continue to perform R&D on various FHE technologies, and NextFlex funds or will fund some of that work.
2. High performance environments characterized by high frequency, high power density, and elevated temperatures continue to be the exclusive domain of inorganic semiconductors.
3. Comparing FHE and conventional electronics is only partially meaningful, because the application domains where each of the two technologies excel do not necessarily overlap in a significant manner at the present time.
4. From the variety of flexible electronics and printed electronics technologies that are currently under development or offered in the market, FHE continues to receive the most attention in terms of near-term commercialization opportunities.

5. Governments from the European Union, Singapore, Japan, Korea, and China have continued to invest in enabling technologies for FHE. The U.S. FHE Manufacturing Innovation Institute should help foster U.S. leadership not only in R&D but in commercialization within this emerging industry, as opposed to the "domestic R&D and outsourced manufacturing" that currently plagues the conventional electronics industry.

6. Qualification of materials and manufacturing processes and equipment is occurring too slowly to meet cost/performance/utility demands and enable near-term product launches.

7. Development of characterization tools and technology, both in-line (metrology) and off-line (quality control), is stagnating. Without the consistent quality these tools enable, the benefits of high rate and large area manufacturing of electronics expected from this technology may not be realized.

8. A more comprehensive set of standards for materials, manufacturing, integration, and maintenance would enable a higher rate of adoption, resulting in a much faster commercial success for FHE enterprises.

9. Life cycle management, including disposal of FHE systems after their useful life, must be a consideration. Single-use devices and short lifetime devices will be the biggest concern from this point of view. Short and long term consequences from the possibility of these devices reaching landfills should be considered. If expensive inks are used on throw away items, can those devices be recycled and ink components, substrates, etc. be reused?

10. FHE systems, like other dual use technologies, are developed and consumed in a global market. This implies that: (1) U.S. companies often collaborate with and are purchased by foreign entities; and (2) there is potential for counterfeit or malicious technology to enter the supply chain. This is highly undesirable for all applications, but it is especially critical for defense applications. In related industries (e.g. aircraft manufacturing), there are processes in place for compartmentalizing technology information and for identifying and managing trusted sources. Similar processes must be carefully implemented for the FHE industry, especially in light of the industry's volatility due to its emerging nature.

11. One possible goal of FHE systems made by combining flexible ICs obtained from conventional semiconductor fabrication processes and flexible printed electronics is for these FHE systems to be agilely designed and produced. Since the supply chains for these two technologies have, at least for now, significantly different delivery times, this agility may be difficult to achieve for new devices unless the industry improves delivery time for newly developed flexible ICs and/or produces and stores sufficient numbers of thinned IC wafers to satisfy the expected demand for frequently used ICs over time.

12. In searching for standards for design, fabrication, assembly, and test, FHE companies often use a combination of private corporate standards, old Mil-standards, and standard processes developed by international firms and academia. There needs to be a concerted effort to develop new international standards (such as those developed by ISO) or adopt and modify (and publish as appropriate) standards and processes that are now being successfully employed. The FHE Manufacturing Innovation Institute could serve as a coordinating agency and a repository for these new standards.

13. The significant number of firms that are engaged in the photovoltaics business and are failing indicates that this is still a risky technology investment, despite the potential

benefits it offers with respect to energy independence and potential lower impact on the environment. Government direct investment in improved energy harvesting and storage technologies and their scale-up for manufacturing through agencies such as DARPA, the service laboratories, academia, and the Title III Program seems more promising than trying to pick winners in the energy marketplace. This will remain the case until non- fossil fueled energy becomes a good economic investment.

14. The reliability of FHE systems in harsh environments, including extreme temperature/pressure, high-humidity, and mechanical fatigue, remains a concern. More durable materials and mechanical processes will need to be developed in order to address this reliability concern.

9.2 Future Expectations for FHE

15. Due to rapid progression of technology, today's capability and toolset for FHE systems covers an extremely wide domain. Hence, FHE can become a victim of its own success: without concerted guidance from defense industry and successful commercial initiatives, it may not find a critical focus or concentrate on critical applications. Therefore the next 5-7 years are crucial for identifying FHE developments in the defense industry, as several "killer applications" need to be identified. These may come from display, biomedical, and sensing applications and may heavily depend on the success of novel packaging solutions and power limits.

16. Even though separate "flexible hybrid" and "conventional" electronics contexts still exist today, a decade from now all conventional solid PCB technologies may be abandoned in favor of purely flexible, ultra-light and compact PCBs developed originally for today's FHE systems. Thus the terminology of FHE may not be around too long as such. As the formal distinction between FHE and conventional PCB based approaches fades away, and more mature and high-performance flexible printed electronic devices and electronic textiles are developed, the available power limits (both harvesting and battery stored) will ultimately decide what can be done with FHE as it is understood today.

17. While polymer substrates are the driver today and are likely to remain so in the short term, electronic textiles may dominate and drive FHE system development in the medium term and may even provide a "killer application" context as it can have a large consumer base to attract investment and relevant activity on many facets of technology development (e.g., biomedical wearables, structural inflatables, mobile computing, energy harvesting). Defense related applications can be accelerated with focus on flexible packaging solutions and rapid advances in battery and solar technology.

18. From the perspective of high performance applications, FHE development should focus heavily on flexible PCB, transfer printed-CMOS or thinned-wafers, and packaging, so that it can rapidly make use of existent technology and devices. This will provide time and space for development of more innovative and capable FHE systems and enable valuable feedback regarding the use and design of FHE, since design tools, manufacturing base, and testing capabilities for FHE systems are not yet fully developed.

9.3 Materials Technologies

19. For materials technologies, there is often a trade-off between higher performing, more rigid, inorganic materials and lower performing, more flexible (both in terms of mechanical

stiffness and manufacturability) organic materials. It is up to the designer to determine which is best for the desired end use of the FHE device. This decision definitely depends on the application, and it is usually very clear whether conventional electronics or FHE should be used for a particular application.

20. The high post-processing temperatures necessary to enhance the performance of ink materials will become an increasingly important near-term problem if more heat- resistant substrates or alternative post-processing methods are not developed and accepted by the market.

21. While sometimes not as easy to process and apply as organic materials, inorganic nanoparticle systems have allowed for the reduction of post-processing temperatures while still maintaining near-bulk materials properties, enabling the development of higher performing electronics on flexible film substrates.

22. There is no clear best choice for flexible substrate materials, as the substrate choice depends on the application. To date, the most popular substrates for FHE are PET and PEN films. However, as single-use/disposable devices become ubiquitous, plastic films may be too costly to use, and they also may not meet certain operating condition requirements, such as extreme temperature stability. Flexible glass and ceramic substrates can more readily meet these extreme operating conditions, but they will be a more costly option for the time being.

23. There is currently a dearth of information regarding characterization and qualification of materials used in the FHE industry (e.g., similar to MIL-HDBK-17 for composites). The FHE Manufacturing Innovation Institute should begin to identify materials of promise and develop new ISO-type handbooks for FHE materials.

9.4 Manufacturing Technologies

24. The industry requires standardized, scalable manufacturing flows that leverage processes developed by the microelectronics, semiconductor, roll-to-roll, and large area processing industries.

25. The creation and adoption of standards would promote the development and implementation of better metrology and ultimately improved process control, which are definitely required for maturation of the FHE industry. However, the adoption of standards can necessitate large investments in acquisition of production/manufacturing equipment, which could be a deterrent to standards adoption. This is why an organization like the FHE Manufacturing Innovation Institute is needed to spearhead this effort (see item 12 under General, above.)

26. Better planning and execution of research, development, and implementation for FHE is required. Scaling up from laboratory trials to pilot and large scale production often requires a large financial investment. Currently, there is a significant amount of investor funding being spent in laboratory phases without sufficient consideration or planning for scale-up and manufacturing processes.

27. Manufacturing lines for large area printed electronics produced via roll to roll processes are controlled with hybrid process control systems using discrete, batch, and closed loop systems. These integrated process control systems, metrology, and lean / agile

manufacturing approaches can be used to resolve in-line manufacturing problems. More focus on process control and metrology for FHE systems can drive manufacturing refinement and eventually reduce production costs and product variability.

28. Most manufacturing approaches to large area electronics are being designed to include stand-alone systems (e.g. printing, post-processing) in conjunction with more standard fab technologies to complete a manufacturing line. This integration is often not optimal, because insufficient emphasis and effort are placed on designing/engineering novel solutions that can prevent loses in production efficiencies.

29. A general, low-cost, and scalable chip transferring/adaptation process that can be used with various materials, including compound semiconductors, is needed for accelerating FHE product development. New tools and manufacturing processes need to be developed that can be used independently of the type of wafer technology.

9.5 Integration and Sustainment

30. Rules for design and standards for packaging and integration of FHE systems are necessary. In particular, the lack of standard methods for interconnecting rigid or flexible ICs with flexible electronics, or connecting FHE devices/assemblies with conventional electronic devices/assemblies easily result in one-of-a-kind configurations that are difficult to manage, maintain, and reproduce.

31. Aircraft applications of FHE systems, for example in conformal antennas, heaters, or other devices, will benefit from effective encapsulation and barriers that protect the electronics from the environment and reduce the potential for failure. When failures do occur, these aircraft mounted FHE systems must be repaired or replaced. Planning and design for maintenance of FHE systems that are adhered to aircraft surfaces is necessary, so that maintenance processes are as efficient and cost effective as those used for conventional electronics. Otherwise FHE technology may actually become a liability for aircraft applications. Maintainability can be crucial for FHE in defense applications unless the aircraft components that integrate FHE are designed to be disposable.

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LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

Acronym/Symbol	Description
DARPA	Defense Advanced Research Projects Agency
DC	direct current
DGU	density gradient ultracentrifugation
DoD	Department of Defense
DOD	drop-on-demand
DOE	Department of Energy
dpi	dots per inch
DRAM	dynamic random access memory
DSSC	dye-sensitized solar cell
DTI	Deposition Technology Innovations
DW	direct write
DWE	direct write electronics
EB	electron beam
ECD	electrochemical deposition
ECG	electrocardiogram
ECR	electron-cyclotron resonance
EDA	electronic design automation
EDLC	electrochemical double layer capacitor
EL	electroluminescent
EM	electromagnetic
EMI	electromagnetic interference
ENAS	Institute for Electronic Nano Systems
EO	electro-optic
EPD	electrophoretic display
EW	electronic warfare
fab	an electronics fabrication facility, or foundry
fab, pure-play	a foundry-only business; that is, an electronic device fabrication business that
fabless	an electronics manufacturer that designs circuits and has them fabricated by
FE	flexible electronics
FEA	finite element analysis
FET	field effect transistor
FHE	flexible hybrid electronics
FHE MII	flexible hybrid electronics manufacturing innovation institute
FM	frequency modulation
foundry or fab	facility that fabricates electronic devices using design provided by customers
FPC	flexible printed circuit
GaAs	Gallium Arsenide
GaN	Gallium Nitride
Ge	Germanium
GEM	Gwent Electronic Materials

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONT'D)

Acronym/Symbol	Description
GHz	gigahertz = one billion (109) Hz
GMR	giant magnetoresistance
GNP	graphene nanoplatelets
GO	graphene oxide
GPS	global positioning system
HDI	high density interconnect
HOPG	highly oriented pyrolytic graphite
HPC	high performance computing
HPCVD	hybrid physical-chemical vapor deposition
I/O	input/output
IAD	ion assisted deposition
IBAD	ion beam assisted deposition
IBIC	Industrial Base Information Center
IC	integrated circuit
III-V	Chemical compounds with at least one group III element and at least one group
IMEC	Interuniversity Microelectronics Centre
iNEMI	International Electronics Manufacturing Initiative
InGaP	indium gallium phosphide
InP	Indium Phosphide
InSb	Indium Antimonide
IoT	Internet of Things
IP	intellectual property
IR	infrared
ISR	intelligence, surveillance, and reconnaissance
ITAR	International Traffic in Arms Regulations
ITO	indium tin oxide
ITRI	Industrial Technology Research Institute
ITRS	International Technology Roadmap for Semiconductors
IVD	ion vapor deposition
Ka-Band	26.5–40 GHz portion of the EM spectrum; part of (just above) the K band of
K-Band	20 to 40 GHz portion of the EM spectrum
Ku-Band	12–18 GHz portion of the EM spectrum in the microwave range of
LAFE	large area flexible electronics
L-Band	1 to 2 GHz range of the EM spectrum, in the radio frequency range
LCD	liquid crystal display
LCP	liquid crystal polymer
LED	Light Emitting Diode
LUMO	lowest unoccupied molecular orbital
MATES	Manufacturing Technology Support
MBE	Molecular Beam Epitaxy
MCM	Microcircuit Materials

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONT'D)

Acronym/Symbol	Description
MCM	multi-chip module
MEMS	micro-electromechanical system
MEMS	micro-electronically machined systems (second definition)
MICE	mesoscopic integrated conformal electronics
MIM	metal-insulator-metal
MIT	Massachusetts Institute of Technology
MLC	multi-level cell
MLD	molecular layer deposition
MMW, mmW	Millimeter Wave
MOCVD	Metal-Organic Chemical Vapor Deposition
MWCNT	multi-walled carbon nanotube
NanoOPS	Nanoscale Offset Printing System
NASA	National Aeronautics and Space Administration
NEMS	nanoelectromechanical systems
NFC	near field communication(s)
NIR	near-IR
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
NSF	National Science Foundation
NSTI	Nano Science and Technology Institute
NTNU	Norwegian University of Science and Technology
NW	nanowire
OE-A	Organic and Printed Electronics Association
OEM	original equipment manufacturer
OFET	organic field effect transistor
OLED	organic light emitting diode
OPV	organic photovoltaic
OTFT	organic thin film transistor
P3HT	poly(3-hexylthiophene)
PAA	poly(acrylic acid)
PARC	Palo Alto Research Center
PC	polycarbonate
PCB	printed circuit board
PCBM	phenyl Cn butyric acid methyl ester
PDMS	polydimethylsiloxane
PE	polyethylene
PE	printed electronics
PECVD	plasma enhanced chemical vapor deposition
PEDOT	poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEEK	polyetheretherketone
PEN	polyethylene naphthalate

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONT'D)

Acronym/Symbol	Description
PET	polyethylene terephthalate
PEUT	polyether urethane
PI	polyimide
PLA	polylactic acid
PLD	pulsed laser deposition
PLED	polymer light emitting diode
PSS	polystyrene sulfonate
PTC	positive temperature coefficient
PTF	polymer thick film
PTFE	polytetrafluoroethylene
pure-play	see fab, pure-play
PV	photovoltaic
PVC	polyvinylchloride
PVD	physical vapor deposition
PVDF	polyvinylidene fluoride
PVP	polyvinylpyrrolidone
PVP	poly-4-vinylphenol
PWB	printed wiring board
PZT	lead zirconate titanate
Quantum computing	study of quantum computers: theoretical computation systems that make direct use of quantum-mechanical phenomena, such as superposition and entanglement, to perform operations on data
R&D	research and development
R2R	roll-to-roll
RAM	random access memory
RCA	Radio Corporation of America
RF	radio frequency
RFI	radio frequency interference
RFID	radio frequency identification
RX	AFRL Materials and Manufacturing Directorate
RXM	AFRL/RX Manufacturing and Industrial Technologies Division
RXME	AFRL/RXM, Electronics and Sensors Branch
SAFC	Sigma-Aldrich Fine Chemical
SALD	spatial atomic layer deposition
S-Band	2 – 4 GHz portion of the EM spectrum
SBIR	Small Business Innovation Research
SCM	single chip module
SEDD	Sensors and Electron Devices Directorate
SEER	salt-enhanced electrostatic repulsion
SEM	scanning electron microscopy/microscope
Si	Silicon
SiC	Silicon Carbide

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONT'D)

Acronym/Symbol	Description
sicelene	a two-dimensional allotrope of silicon, with a hexagonal honeycomb structure similar to that of graphene
SiF	system-in-foil
SiGe	Silicon germanium
SiGe:C	Silicon germanium with added carbon
SMA	shape memory alloy
SMA	sub-miniature version A
SMEA	stretchable microelectrode array
SMT	surface mount technologies
SoC	system on chip
SOI	silicon-on-insulator
SSLR	solid state laser reflection
STTR	Small Business Technology Transfer
SUNY	State University of New York
SWaP	size, weight, and power
SWaP	size, weight and power
SWaPc	size, weight and power and cost
SWCNT	single walled carbon nanotube
SWeNT	SouthWest NanoTechnologies
TCF	transparent conductive film
TCO	transparent conductive oxide
TCR	temperature coefficient of resistance
technology	The minimum half pitch of metal interconnects in an electronic device
TENG	triboelectric nanogenerator
TFT	thin film transistor
Tg	glass transition temperature
THz	terahertz = one trillion (1012) Hz
TI	Texas Instruments
Title III	Defense Production Act (DPA) Title III Program; its mission is to "create assured, affordable, and commercially viable production capabilities and capacities for items essential for national defense"
Tri-gate	a 3D transistor fabrication technology used by INTEL Corporation.
UAV	unmanned air vehicle
UCLA	University of California at Los Angeles
UTC	Universal Technology Corporation
UV	ultraviolet
V-Band	40 – 75 GHz portion of the EM spectrum, in the millimeter wavelength range
VOC	volatile organic compound
W-Band	75 – 110 GHz portion of the EM spectrum, in the millimeter wavelength range
WBG	wide bandgap

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS (CONT'D)

Acronym/Symbol	Description
WPAFB	Wright-Patterson Air Force Base
WVTR	water vapor transmission rate
X-Band	8.0 – 12.0 GHz portion of the EM spectrum